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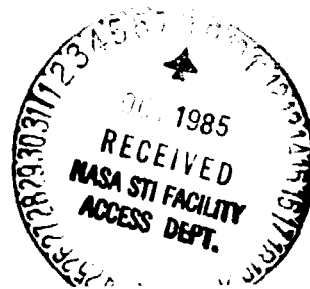
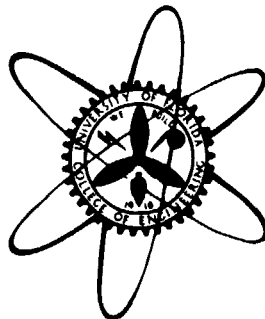
FINAL REPORT
ON
RESEARCH ON SOLAR PUMPED LIQUID LASERS

NAG-1-135

BY

JOHN D. COX, ULRICH H. KURZWEG, NEIL H. WEINSTEIN
AND
RICHARD T. SCHNEIDER

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Gainesville

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I. INTRODUCTION

The goal of this research effort was to develop a solar pumped liquid laser that can be scaled up to high power (10MW CW) for space applications. Liquid lasers have the inherent advantage over gases in that they provide much higher lasing densities and thus high-power densities. Liquids also have inherent advantages over solids in that they have much higher damage thresholds and are much cheaper to produce for large scale applications.

Among the liquid laser media that are potential candidates for solar pumping, the $\text{POCl}_3:\text{Nd}^{3+}:\text{ZrCl}_4$ liquid has been chosen for its high intrinsic efficiency as well as its relatively good stability against decomposition due to protic contamination. The research effort has been devoted towards the development of a manufacturing procedure and performance testing of the laser liquid as well as the development of an inexpensive large solar concentrator to pump the laser.

Specifically our efforts have been devoted to the following areas:

1. Laser liquid preparation and handling:

- a) $\text{POCl}_3:\text{Nd}^{3+}:\text{ZrCl}_4$
- b) Cr^{3+} doped $\text{POCl}_3:\text{Nd}^{3+}:\text{ZrCl}_4$

2. Diagnostics:

- a) Laser solution quality (spectroscopic)
- b) Nd^{3+} upper state lifetime

3. Laser performance parameters:

- a) Gain (flashlamp)
- b) Lasing threshold (flashlamp pumped)
- c) Solar simulator experiment

4. Solar concentration facility

a) Mirror fabrication

i) spin cast

ii) inflatable

b) Mirror performance characteristics

i) concentration factor

ii) total power

c) Solar pumped laser (Nd^{3+} :YAG)

II. PREPARATION OF THE LIQUID LASER MEDIUM

A. General Concept

The objective of this project element has been to prepare an aprotic solution containing 0.3M Nd^{3+} ion suitable for lasing. It is necessary that the solution be aprotic to avoid non-radiative quenching of the excited state. We chose the system which results from dissolving neodymium trifluoroacetate in phosphorus oxychloride (POCl_3) with the aid of zirconium tetrachloride (ZrCl_4). The choice of this solution in preference to other similar solutions was based on the relative stability of this solution, both under operating conditions and toward minor accidental water contamination. Phosphorus oxychloride was the preferred solvent because it is less corrosive and less toxic than selenium oxychloride (SeOCl_2). The system employing POCl_3 with ZrCl_4 as the Lewis acid is stable to UV radiation and, therefore, does not photodegrade. It has the additional advantage that ZrCl_4 reacts with water to produce a solid (ZrOCl_2) and a gas (HCl), thereby removing protic contamination from the solution.

B. Previous Difficulties

We believe that our initial difficulties in affecting solution--we initially obtained large amounts of precipitate--were due to a combination of factors. These included "wet" POCl_3 (it still contained in excess of 75 ppm's of protic species), wet ZrCl_4 , and handling techniques which were not sufficiently rigorous to maintain anhydrous conditions. These were corrected by treating the POCl_3 with lithium metal, purchasing a new supply of ZrCl_4 , and designing a new distillation apparatus which incorporated the use of syringe techniques to make all transfers. We had been reluctant to make the first of these changes--the use of lithium to decontaminate the POCl_3 of protic species--because drying POCl_3 with other alkali metals (e.g., Na or K) is reported to frequently result in an explosion. However, it was pointed out to us by the GTE group that the use of lithium was absolutely necessary to get the solvent sufficiently free of protic contamination. The other improvements were necessary to keep the solution free of protic contamination. What follows is a detailed procedure--including diagrams of our glassware--which may be used to produce the required lasing solution.

C. Reagents

The following reagents were purchased and used as received:

neodymium oxide, Nd_2O_3 (99.999%, Alfa Products),
trifluoroacetate acid, CF_3COOH (TFA) (reagent grade,
Fisher Scientific Co.), and
zirconium tetrachloride, ZrCl_4 (99.9%, Research Organic/
Inorganic Chemical Corp.).

The phosphorus oxychloride, POCl_3 (reagent grade, Fisher Scientific Co.), was treated as described in a following section or purchased and used as received if Suprapur (MCB).

Lithium metal, Li (99.9%, Alfa Products), was obtained as shot, packed under argon with a coating of mineral oil on it. The mineral oil was removed by washing the metal with hexane (or other low boiling hydrocarbon) and collecting the lithium on a filter. The metal was then air dried (quickly, to avoid nitride formation) and transferred to a vacuum dessicator where the last traces of protic contamination (i.e., the hexane) were removed. The use of lithium dictates the use of argon for the inert atmosphere in subsequent distillations. The argon gas, Ar (99.998%, Airco) was always dried by passing it through a column of indicating Drierite (W.A. Hammond Drierite Co.) and Aquasorb (Mallinckrodt) before being used.

Anhydrous neodymium trifluoroacetate, $[\text{Nd}(\text{CF}_3\text{COO})_3]$, was made by very SLOWLY adding 170 ml of trifluoroacetate acid to a mixture of ~50 g (accurately weighted) of Nd_2O_3 and 100 ml of water. The mixture was stirred, then heated until all of the Nd_2O_3 dissolved. Water and excess TFA were then removed by evaporation, leaving a dark lavender solid, hydrated $\text{Nd}(\text{TFA})_3$. The solid was then ground up and transferred to a vacuum oven to be dried to constant weight. This took several weeks with the oven operating at $\sim 60^\circ\text{C}$. It was necessary to remove the solid from the oven periodically to regrind it and to expose a fresh surface. The theoretical yield (based on exactly 50 grams of Nd_2O_3) is 143.62 g. However, some loss does occur during the many transfers of the solid. The final product, anhydrous neodymium trifluoroacetate, is a pale blue-lavender colored powder.

D. Glassware

Much of the glassware was fabricated to our specifications. Greasing of stopcocks and joints was avoided by the use of Teflon stopcocks throughout and Clear Seal (Wheaton Scientific) joints wherever possible. Teflon tape was used on all other joints to insure a tight fit. (Fluorinated greases should

be avoided since they tend to absorb small amounts of water.) All glassware was routinely cleaned in chromic acid, rinsed, and oven dried at 120°C. In order to avoid contamination from atmospheric moisture, the glassware was removed from the oven immediately before it was used and assembled in our hood while still warm. Care must be taken to only loosely screw on the Teflon stockcocks initially, thus preventing the glass from cracking as it contracts. Only after the glass has cooled should they be tightened completely. The various distillation setups were each wrapped with glass wool to aid in maintaining uniform and constant temperature over the course of the distillation. The connections between glass pieces were made with Teflon-lined polyethylene tubing (e.g., between the still and the bubbler). We used two mineral oil bubblers, each with a check valve. Each opening for syringe entry was capped with a 14 mm rubber septum.

E. Preliminary Treatment of the Solvent

Two consecutive simple distillations of the POCl_3 should be performed under an atmosphere of argon. Only minimal precautions were taken at this stage to insure dryness. Each time only the middle fraction, boiling range 107.5°-108.0°C, was collected (lit. bp = 107.7°C²). This was done to remove HCl, most of the water, and some of the higher boiling impurities. It is important to do this before adding the lithium metal to minimize the reaction between the lithium and the more reactive protic species. If the distillate was completely colorless, it was transferred to the final distillation apparatus (Figure 1) and the lithium metal was added. (CAUTION: In one instance, when the POCl_3 was slightly yellowish, an explosion occurred after the lithium had been added. We speculate that this may have been caused by a volatile impurity which catalyzed a reaction between the lithium and the POCl_3 .) From this point on, all operations were conducted under an atmosphere of argon.

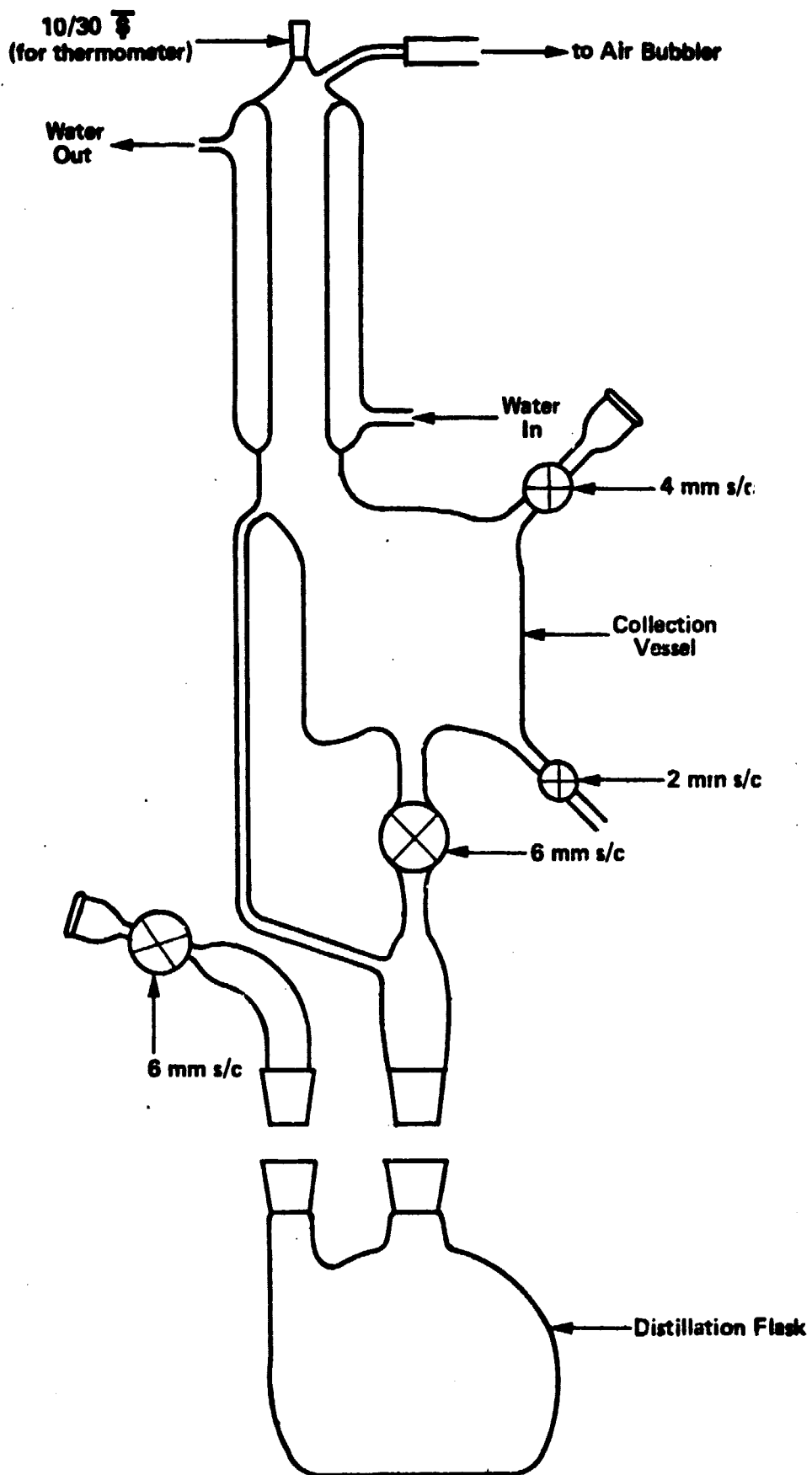


Figure 1: POCl_3 Reflux/Distillation Apparatus

F. Preparation of the Pure Solvent

The POCl_3/Li mixture was then refluxed for 24 hours. This allowed the solvent to remove traces of water from the walls by "washing" the glassware. When the POCl_3 returned to the distillation flask, the lithium reacted with any water present and also any protic species which had been formed by reaction with water, further drying the apparatus. Phosphorus oxychloride was then distilled into the collection vessel by closing the 6 mm stopcock. After a first cut was removed through the 2mm stopcock, the pure, dry POCl_3 was collected. (Since our condensing column was too close to the thermometer in this apparatus, exact temperature readings were not used as a guide in distilling pure solvent.)

G. Preparation of the Lasing Liquid

The apparatus as seen in Figure 2, connection scheme (1) was taken into a glove bag. Anhydrous neodymium trifluoroacetate (14.5 grams, 0.030 moles) and a magnetic stirbar were placed in the bottom of the reaction flask. Zirconium tetrachloride (10.5 grams, 0.045 moles) was placed in the solid addition funnel. The connection to the argon bubbler was protected with a rubber bulb and the flask was removed from the glove bag to the hood where a second argon bubbler was connected. Using a double-tipped needle, opening (A) (Figure 1) was connected to opening (B) (Figure 2). Gas pressure was used to transfer 100 ml of POCl_3 to the reaction flask. The mixture was stirred and some solid remained until the ZrCl_4 was added by rotating the solid addition funnel. In some cases, it may have been necessary to allow the solution to flow into the addition funnel to get all of the ZrCl_4 out of it. The order of reaction, mixing POCl_3 with $\text{Nd}(\text{TFA})_3$ and then adding ZrCl_4 is contrary to all published accounts of the preparation, but it is in accord with our direct communications with one of the original workers on the project at GTE.

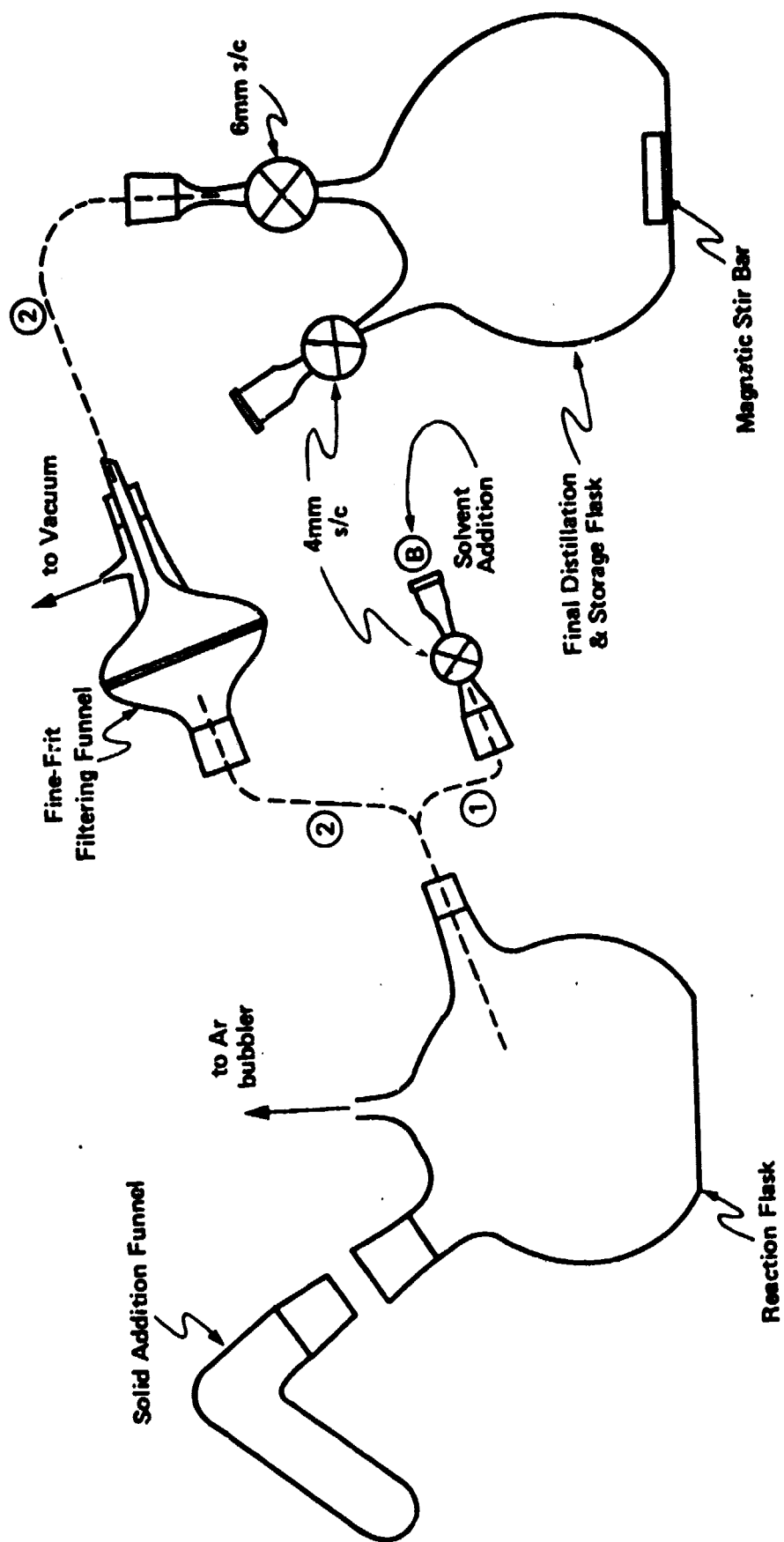


Figure 2: $\text{POCl}_3:\text{Nd}^{3+}:\text{ZrCl}_4$ Preparation Apparatus and Storage Flask

When it appeared as if all of the solid had dissolved, the filtering funnel and the final distillation/storage flask were attached (see Figure 2, connection scheme (2)). The apparatus was then tipped to allow for filtering and the solution was collected in the "final distillation" flask. This flask was then attached to a simple distillation set up and the solution was distilled to one-half volume (50 ml) to remove volatile impurities that had accumulated over the many steps. The solution was then reconstituted to 100 ml by adding fresh POCl_3 , using a double-tipped needle as before. The solution was stored in this flask.

H. Handling of the Laser Liquid

As shown in Figure 2, the storage flask is sealed by two Teflon stopcocks, yet there is still access to the solution--without exposing it to air--through a rubber septum. We believe that this is sufficient protection for prolonged storage of the solution. However, we have not attempted to store a solution in this flask for longer than three months. Therefore, prolonged storage in this manner has not been fully tested.

As needed, a portion of the solution was removed with a 50 cc syringe and transferred to the laser cavity. The laser cavity which we used for all the data presented in this report was made by melting a Pyrex tube around the edges of both quartz windows. Since the quartz had not been melted, this procedure did not afford a complete seal and there was some leakage where the quartz and the Pyrex met. Apparently, the incomplete seal also allowed water to get into the cavity resulting in the formation of some precipitate. Over a period of time the viscosity and turbidity of the solution increased significantly, preventing the successful alignment of the laser cavity and mirrors. We believe that the presence of water was also responsible for a pressure build up, (possibly HCl gas) within the cavity. The increased pressure only

became a problem while opening the laser cavity. We believe that we have since corrected both of these problems by changing to an all Pyrex cavity having windows which are fused onto the main body of the cavity.

III. THE Cr³⁺ DOPED LASER LIQUID

The successful preparation of a Cr³⁺ doped laser liquid has been accomplished. The concentration of Nd³⁺ ion is 0.3 molar and the Cr³⁺ is 2×10^{-3} molar. The concentration of the Nd³⁺ ion is the same used in all other data-lines and has been reported in the literature to be optimum. The concentration of the Cr³⁺ which ion has been successfully used in the emerald and Alexandrite lasers range from of 0.1 M to 10^{-4} molar.

In the first set of experiments to measure lifetime and lasing threshold, no significant improvement in the performance of the liquid was noted. The lifetime of the Nd³⁺ upper laser state has been measured to be 150 μ sec and the lasing threshold at about 110 Joules (98% output coupler). However, after each pulse, bubbles formed in the laser cell which subsequently rose to the top of the cell. These bubbles have not been observed before. They might indicate that the chemistry between Cr³⁺ ions and the solution has not come to equilibrium (as noted before in other Cr³⁺ ion containing solutions).

Our investigations of methods to dope the lasing liquid with Cr³⁺ have focused exclusively on the use of Cr(TFA)₃. While Cr(TFA)₃ is readily soluble in POCl₃, we anticipated problems because we initially believed that the Cr(TFA)₃ (bought from PCR Research Chemicals, Inc.) was "wet" based on the initial IR; see Figures 3 (solid) and 4 (POCl₃ solution) and that somewhere during the preparation of the doped laser solution we would need to dry it. The electronic spectrum of the POCl₃ solution was also recorded (Beckman DB-G) for later comparison (Figure 5).

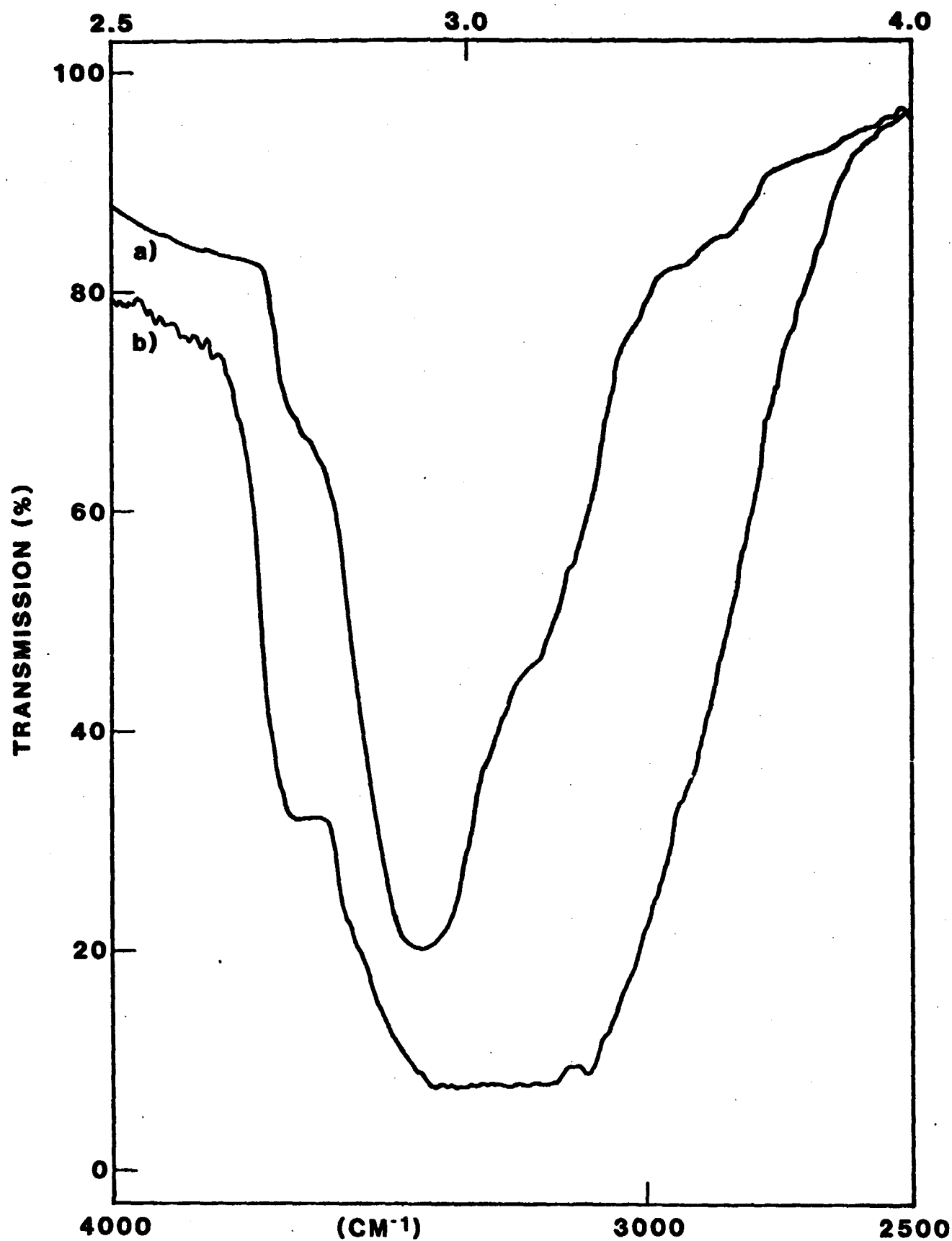
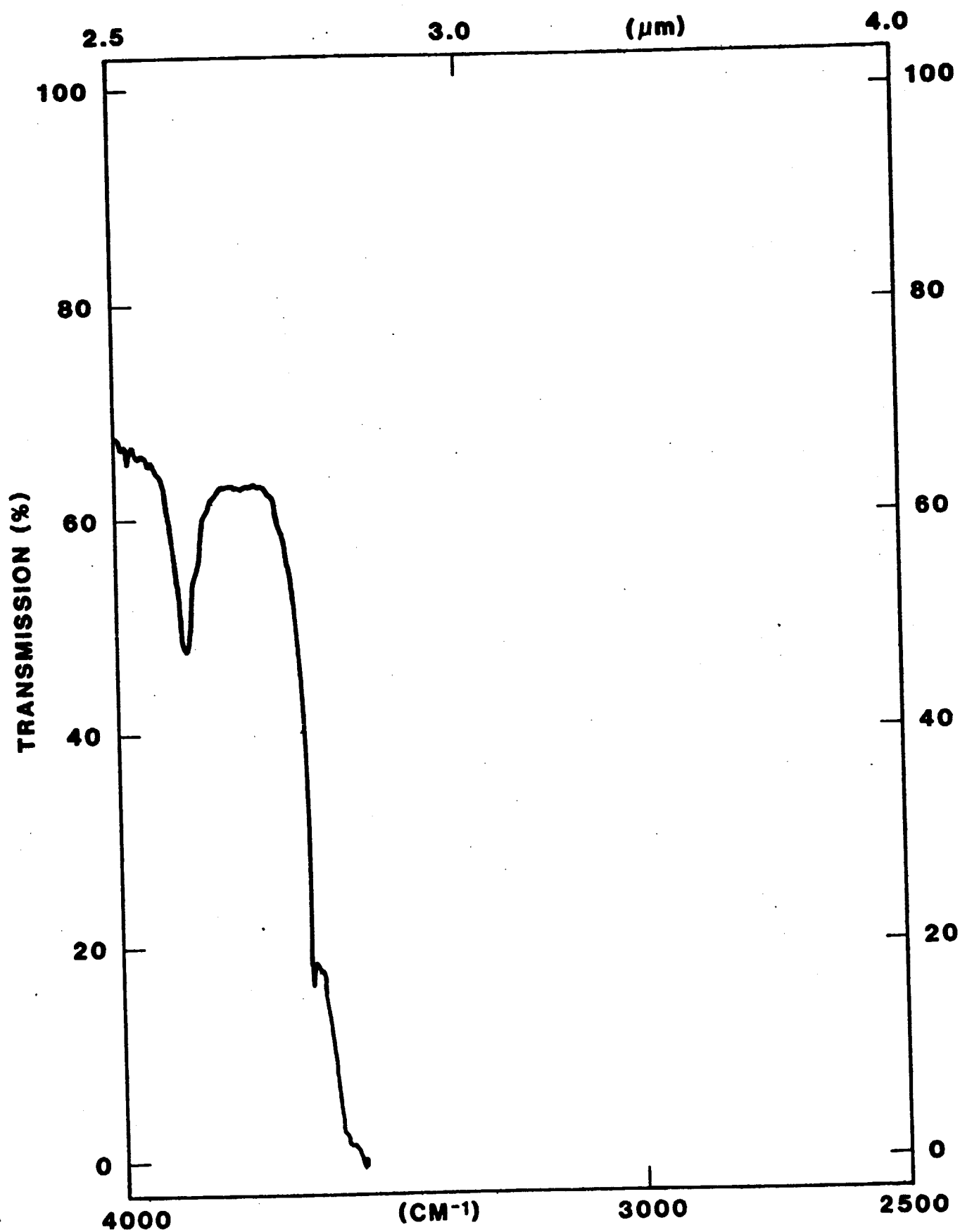


Figure 3: IR of Solid Metal Trifluoroacetates (KBr disk)
a) $\text{Nd}(\text{TFA})_3$, as prepared
b) $\text{Cr}(\text{TFA})_3$, as received



IR of Cr(TFA)₃ in POCl₃

Figure 4:

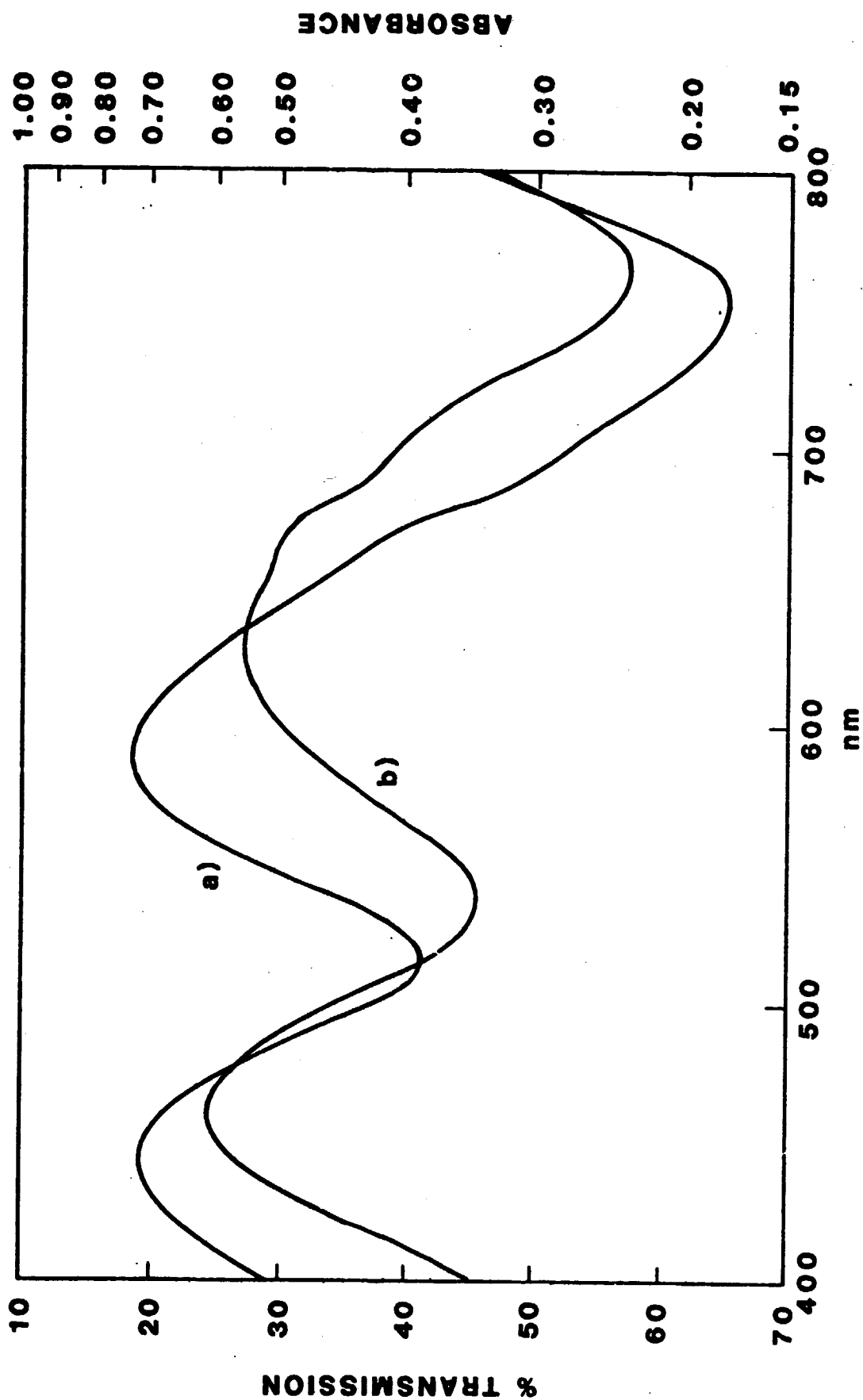


Figure 5: Electronic Absorption Spectrum of $\text{Cr}(\text{TFA})_3$ in POCl_3

a) when prepared

b) 11 days later

Our efforts to dry the chromium compound centered around combining the supposed " $\text{Cr}(\text{TFA})_3 \times \text{H}_2\text{O}$ " with ZrCl_4 (as the drying agent) in POCl_3 . (We felt that until the chromium was dry, the presence of neodymium would only complicate the interpretation of our observations.) Then, when the solution had been dried, a small amount of this pre-prepared Cr^{3+} containing solution could be added to the normal Nd^{3+} laser solution.

The POCl_3 solution, 0.030M in $\text{Cr}(\text{TFA})_3$ and 0.045M in ZrCl_4 , was dark green when prepared. (The color of a POCl_3 solution containing only $\text{Cr}(\text{TFA})_3$ is bright green.) Within two days, when the first IR (see Figure 6) and visible (see Figure 7, run on PE 330) spectra were run, the color had changed to blue-violet. We monitored this $\text{Cr}(\text{TFA})_3/\text{ZrCl}_4/\text{POCl}_3$ mixture periodically by both IR and visible spectra. The first indication of a change in the solution was the change in peak intensities—including the appearance of a new peak at 810 nm—in the visible spectrum. Since at this time we still thought that the solution was "wet," we doubled the amount of ZrCl_4 , in an attempt to dry it. The mixture was filtered to remove precipitation but there was no noticeable change in the liquid.

However, when we discovered (by following the neodymium laser solution preparation by IR, that what we were seeing in the IR of the chromium trifluoroacetate was not necessarily water but might be the first overtone of the C=O vibration of the CF_3COO^- ion (and probably some water—note the broader absorption band in Figure 3A relative to Figure 3B), we refluxed the solution for one-half hour to facilitate the reaction of ZrCl_4 with water (if there was indeed some there) and to aid the formation and removal of CF_3COCl . The mixture was again filtered and the spectra were run after a total of 10 weeks from the initial addition of $\text{Cr}(\text{TFA})_3$ and ZrCl_4 . The IR (Figure 6) showed significant improvement—a decrease in the content of unwanted species—but more improvement is still necessary before it can be used to dope into the

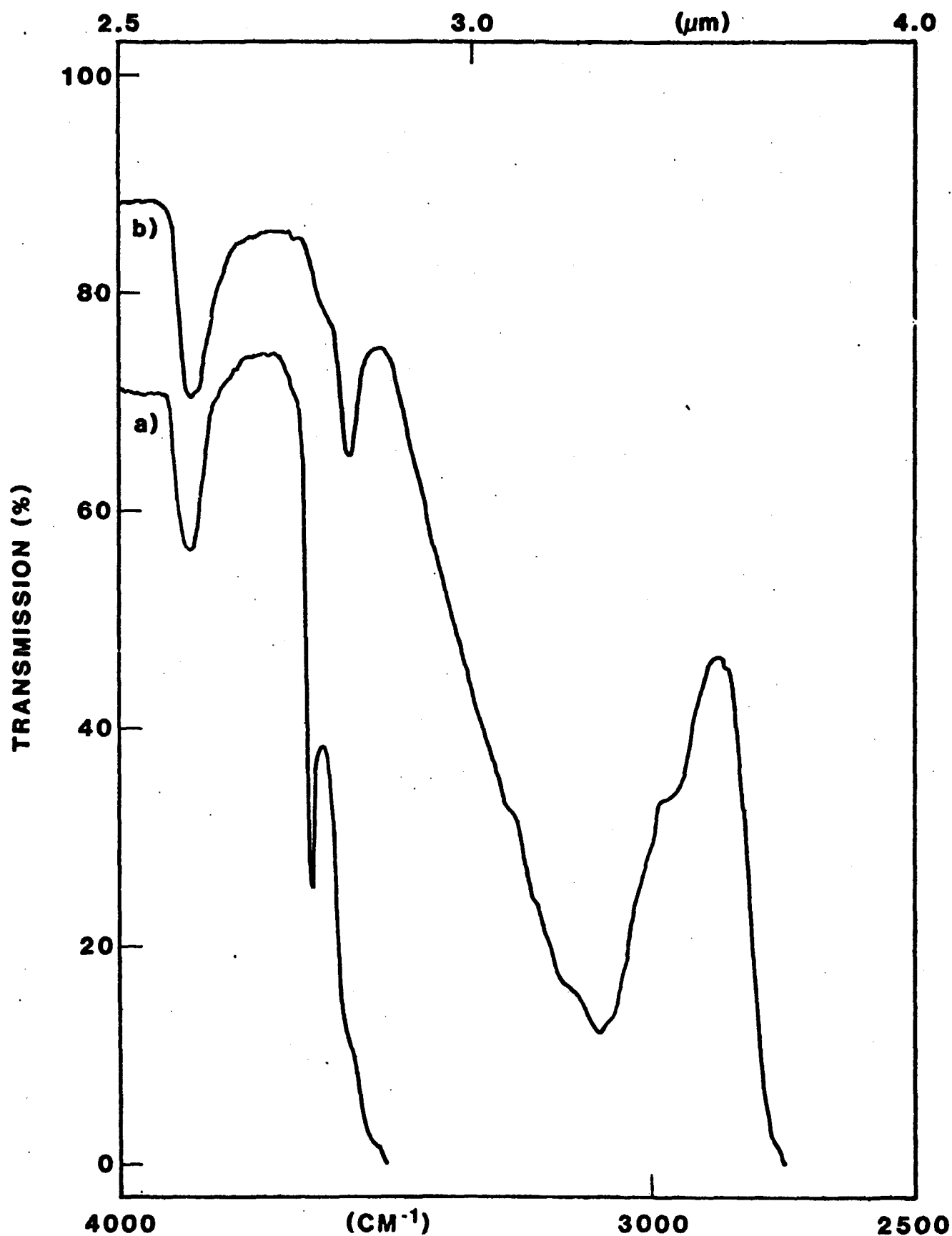


Figure 6: IR of $\text{Cr}(\text{TFA})_3$ and ZrCl_4 in POCl_3

a) shortly after preparation

b) after 10 weeks

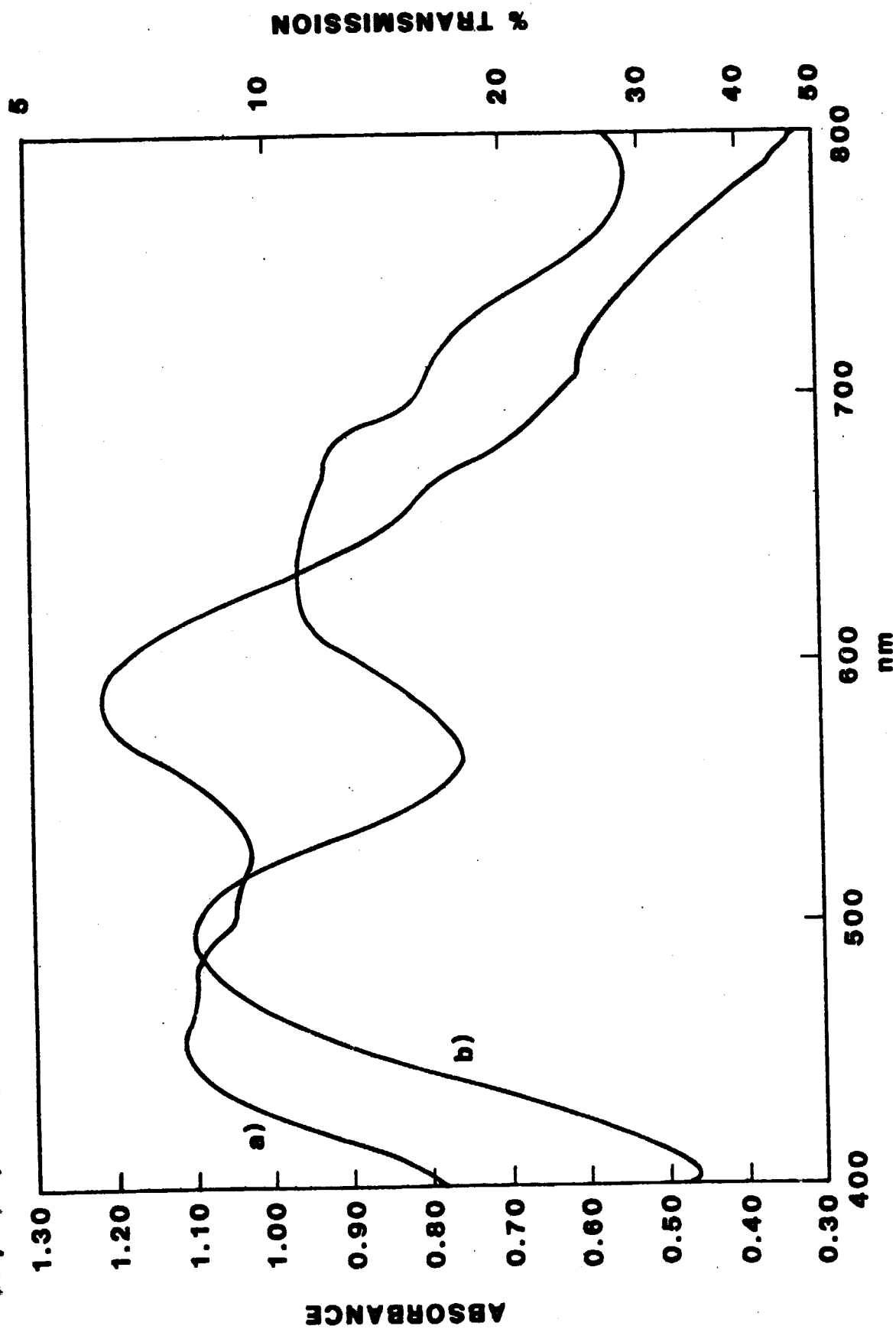


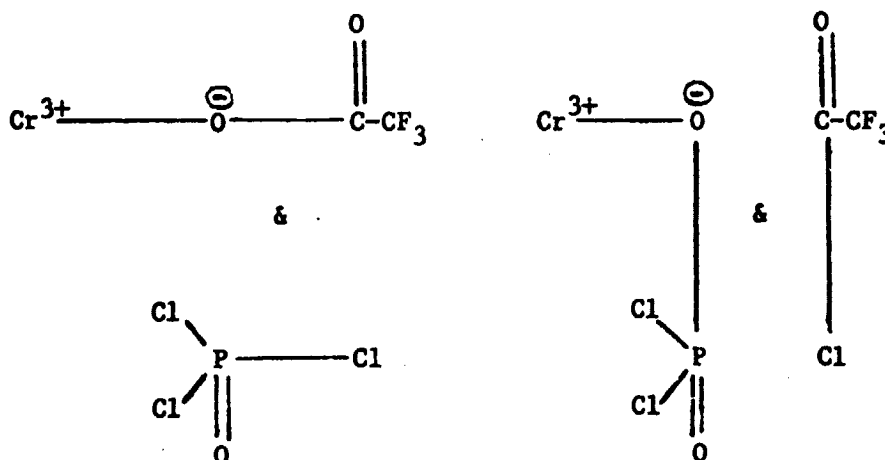
Figure 7: Electronic Absorption Spectra of $\text{Cr}(\text{TFA})_3$ & ZrCl_4 in POCl_3

a) shortly after preparation

b) after 10 weeks

neodymium solution. We found that the visible spectrum (Figure 7, run on Beckman DB-G) also changed considerably. The appearance of an absorption band growing in at 710 nm with time suggests that there is a strong possibility of Cr-Cr interaction developing in the solution. This band might correspond to excitation from the quartet ground state to a doublet state. Such interaction could lead to self-quenching of the excited state. This would be consistent with our inability to observe fluorescence in the 600-800 nm region, although at this stage of purification, other reasons for lack of fluorescence are also possible.

It is also not certain that the final positions of the chromium visible absorption bands will correspond to chromium emission bands that will be suitable for resonance transfer to neodymium. The spectrum of Cr^{3+} doped into Nd:YAG is included for comparison (see Figure 8). While the lack of similarity between the spectrum of Cr^{3+} in YAG and in this POCl_3 doping because it is both necessary and difficult to remove the TFA from the chromium-containing solution. However, once we understood the problem of C=O absorption we did not expect to be able to make as much progress as we did toward removing this obstacle. Also, TFA does possess one possible advantage, in that, since Cr^{3+} exchanges ligands slowly, the reaction occurring in the solution may not involve the breaking of any chromium bonds. That is, the reaction



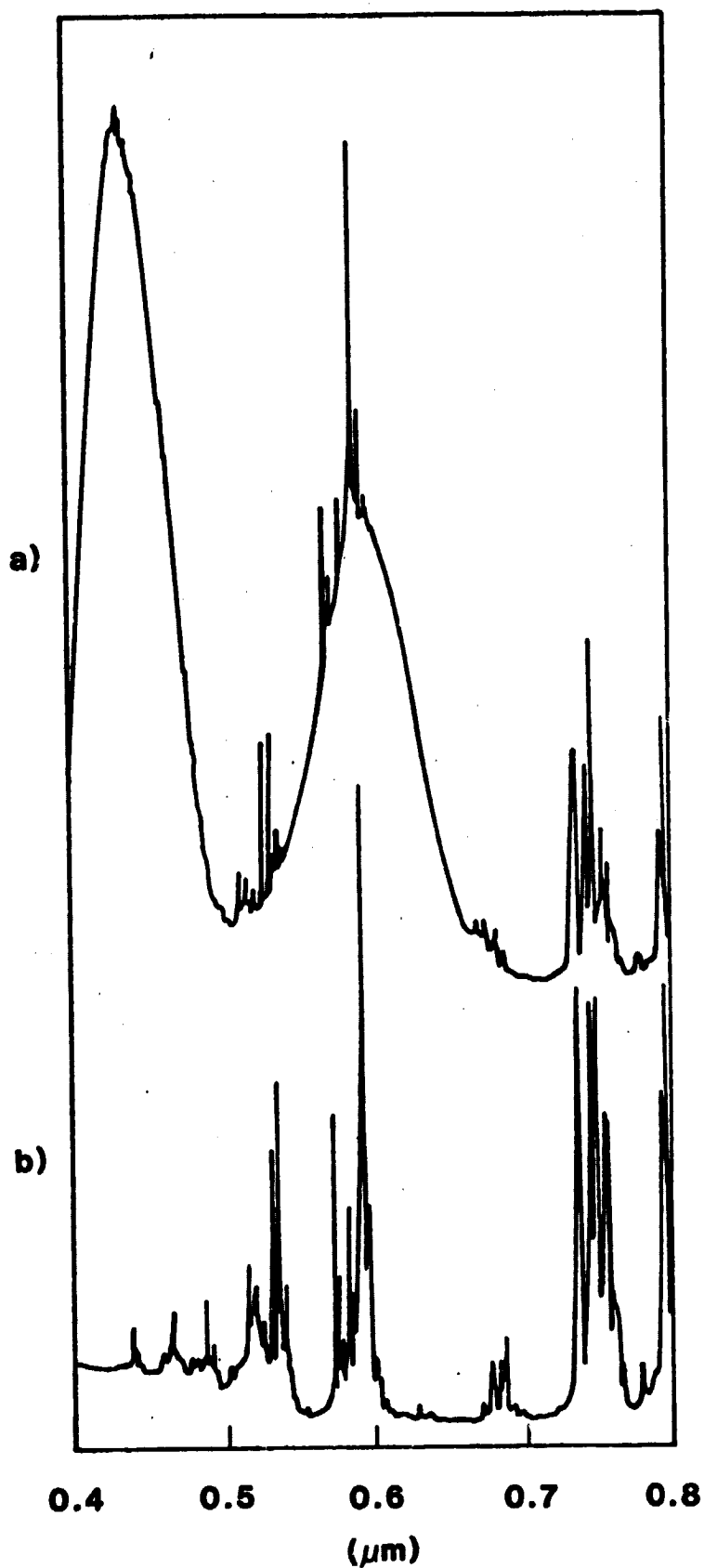


Figure 8: Electronic Absorption Spectra of
a) Cr^{3+} doped in Nd:YAG
b) Nd:YAG

may occur. This allows for the formation of the $\text{Cr}^{3+}\text{-PO}_2\text{Cl}_2^-$ species without breaking the Cr-O bond, a slow step. Therefore, a better choice of counter ion is not obvious at this time.

Chromium doping, in general, may not be the best way to try to enhance the efficiency of the laser because of the possible Cr-Cr interaction. All in all we believe that this approach is not going to provide success in a liquid environment. We observed that the envelope of electronic transitions for Cr^{3+} broadened out significantly in solution and that the intensity of the transitions decreased. We believe that this problem may be inherent to all transition elements. This is in contrast to the f-f transition of the rare earth elements which only lose their fine structure without broadening the entire envelope because the f orbitals are more deeply buried.

In order to increase the electronic energy absorbed by the solution one should look toward doping with those rare earth elements which are capable of transferring energy into the Nd^{3+} manifold, i.e., absorptions involving d-d transitions should be avoided in solution in favor of those involving f-f transitions and the same concept behind the "alphabet YAG" laser should be employed. The alphabet YAG concept when transformed into a solution laser would gain in absorption quality due to the loss of fine structure in the bands.

IV. DIAGNOSTICS

A. Spectroscopic Analysis

The use of infrared spectroscopy ($4000 \rightarrow 2500 \text{ cm}^{-1}$) to check the purity of the solvent was initiated in late 1981 (and used routinely for this purpose thereafter), as well as to check the purity of the final laser solution.

Although we also ran an IR spectrum on $\text{Nd}(\text{CF}_3\text{COO})_3$, we did not have a published spectrum to compare with it, as we did for the POCl_3 (1) and the final laser solution (2). We could only assume that our $\text{Nd}(\text{TFA})_3$ spectrum was free of impurities and reasonably accurate.

1. The Solvent

With regard to the starting solvent we were never able to distill POCl_3 , transfer it to an IR cell, and obtain an IR spectrum that was free of additional adsorption peaks in the region $4000 \rightarrow 2500 \text{ cm}^{-1}$, compared to either the GTE published spectrum (1) or our cleanest spectrum—one run on lot 4M14 of MCB suprapur solvent without any treatment (see Figure 9a). However, the suprapur solvent was not of consistent purity as shown by the IR spectrum of another lot (see Figure 9b). Even our "good" spectrum of POCl_3 contains an extraneous peak at 2280 cm^{-1} —not present in any other spectrum of POCl_3 —which may be only the result of unmatched IR cells.

The differences, some of them significant, which we observed between our spectra and the GTE spectrum were examined. All of our spectra show a well-defined peak at 3860 cm^{-1} compared to a very ill-defined peak in the published spectrum (1). Also, our "good" spectrum shows less absorption and is flatter from $3750 \rightarrow 3150 \text{ cm}^{-1}$ than the published spectrum. Each of our spectra show a small, but sharp drop at 3130 cm^{-1} caused by a grating change in the spectrometer, a Perkin-Elmer 283. The grating change affected the two beams of the double beam instrument differently and resulted in a shift in the observed absorbance—the amount of shift varied from sample to sample. The published spectrum shows a small peak at $\sim 3100 \text{ cm}^{-1}$. We observe this peak (at 3070 cm^{-1}) as well as another peak (at 2940 cm^{-1})—not clearly seen in the published spectrum which used a shorter path length cell—the varying intensity of which (compare Figures 10a and 10b) casts doubt on its inherentness to

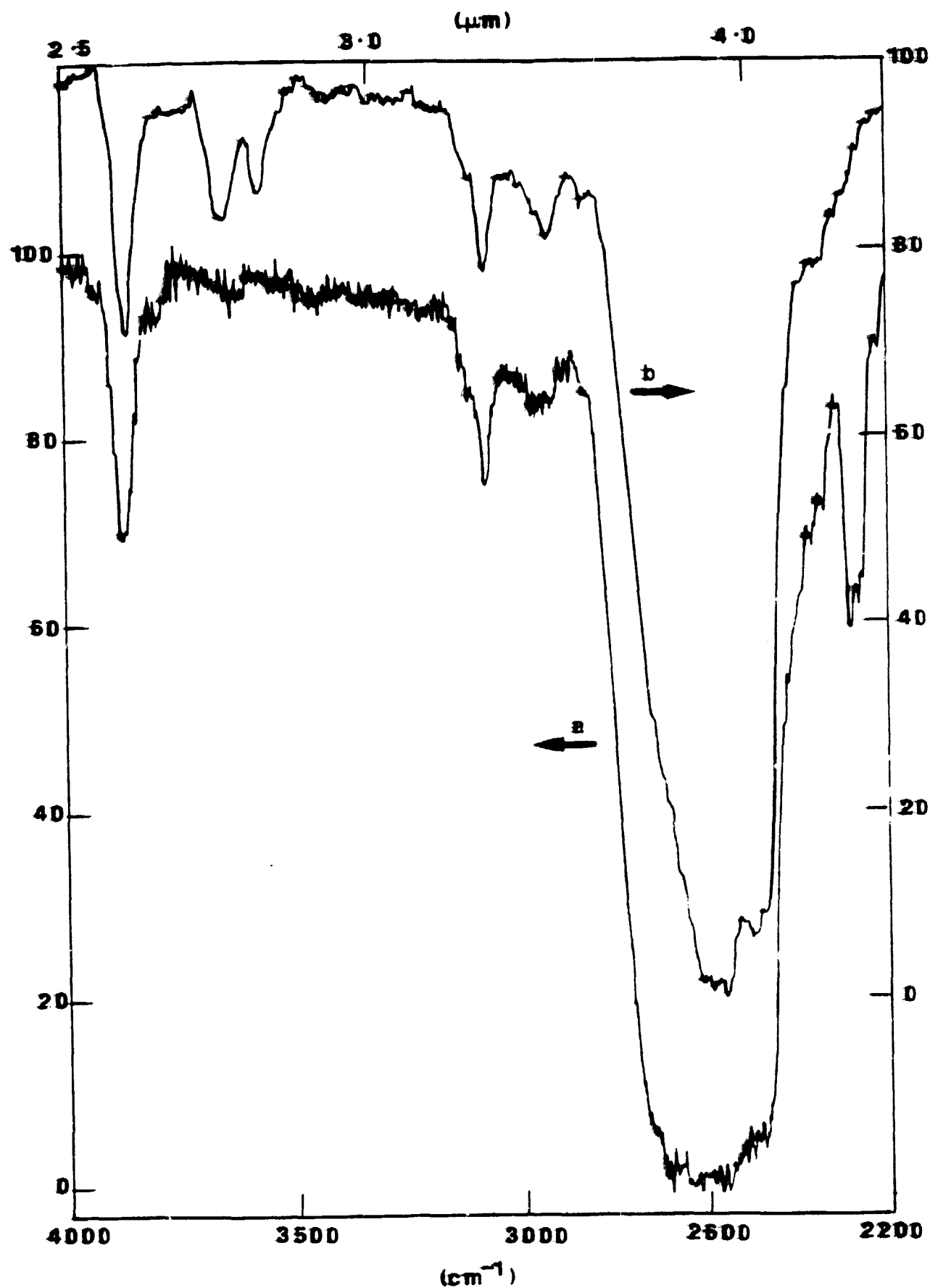


Figure 9: a) Suprapur POCl_3 , as received, lot 4M14
b) Suprapur POCl_3 , as received, lot 2470-614

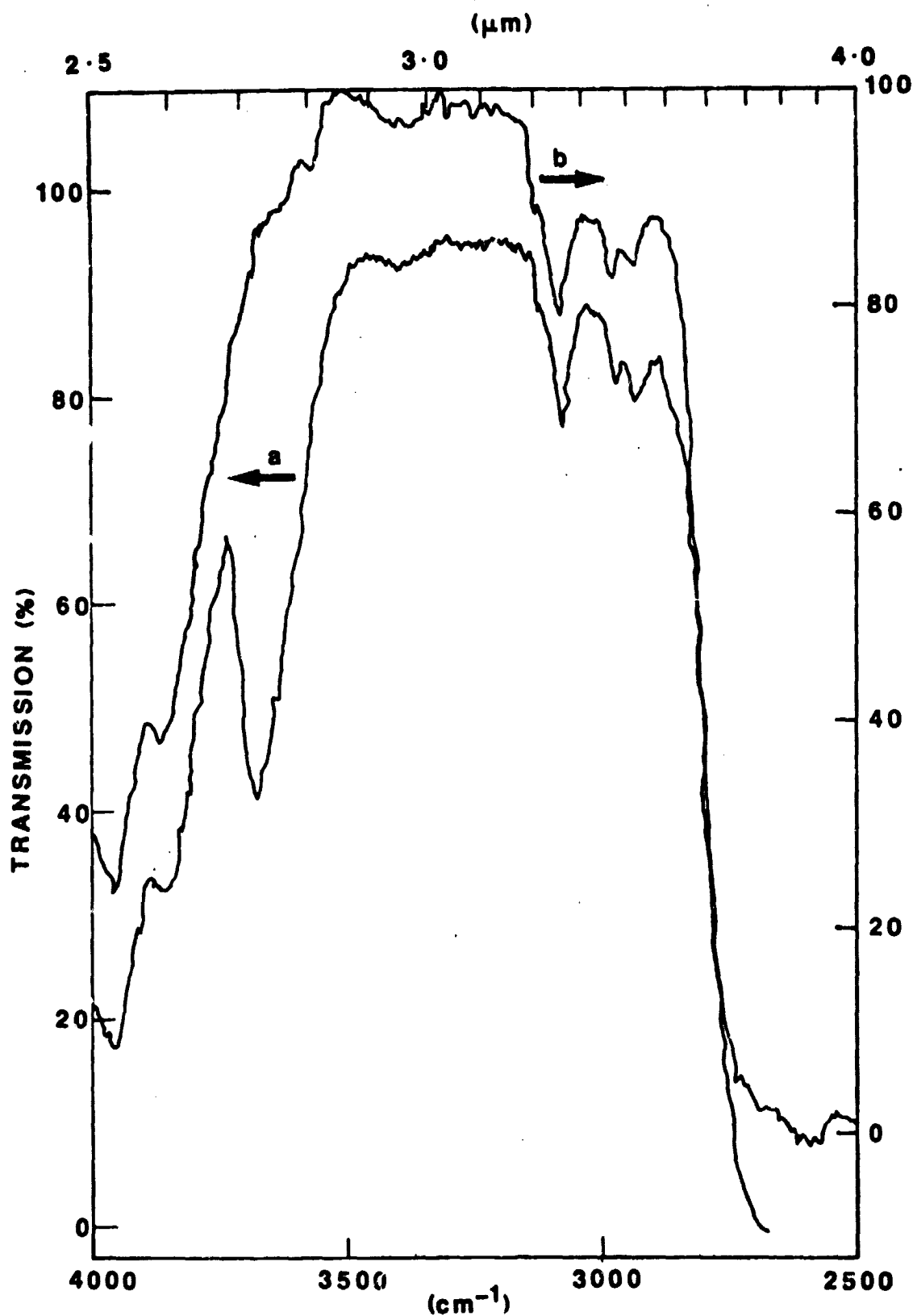


Figure 10: a) The Laser Solution with $t_{1/2} = 280 \mu\text{sec}$.

b) A Laser Solution with $t_{1/2} = 140 \mu\text{sec}$.

Note: A different window material accounts for the peak at 3680 cm^{-1} in spectrum (a).

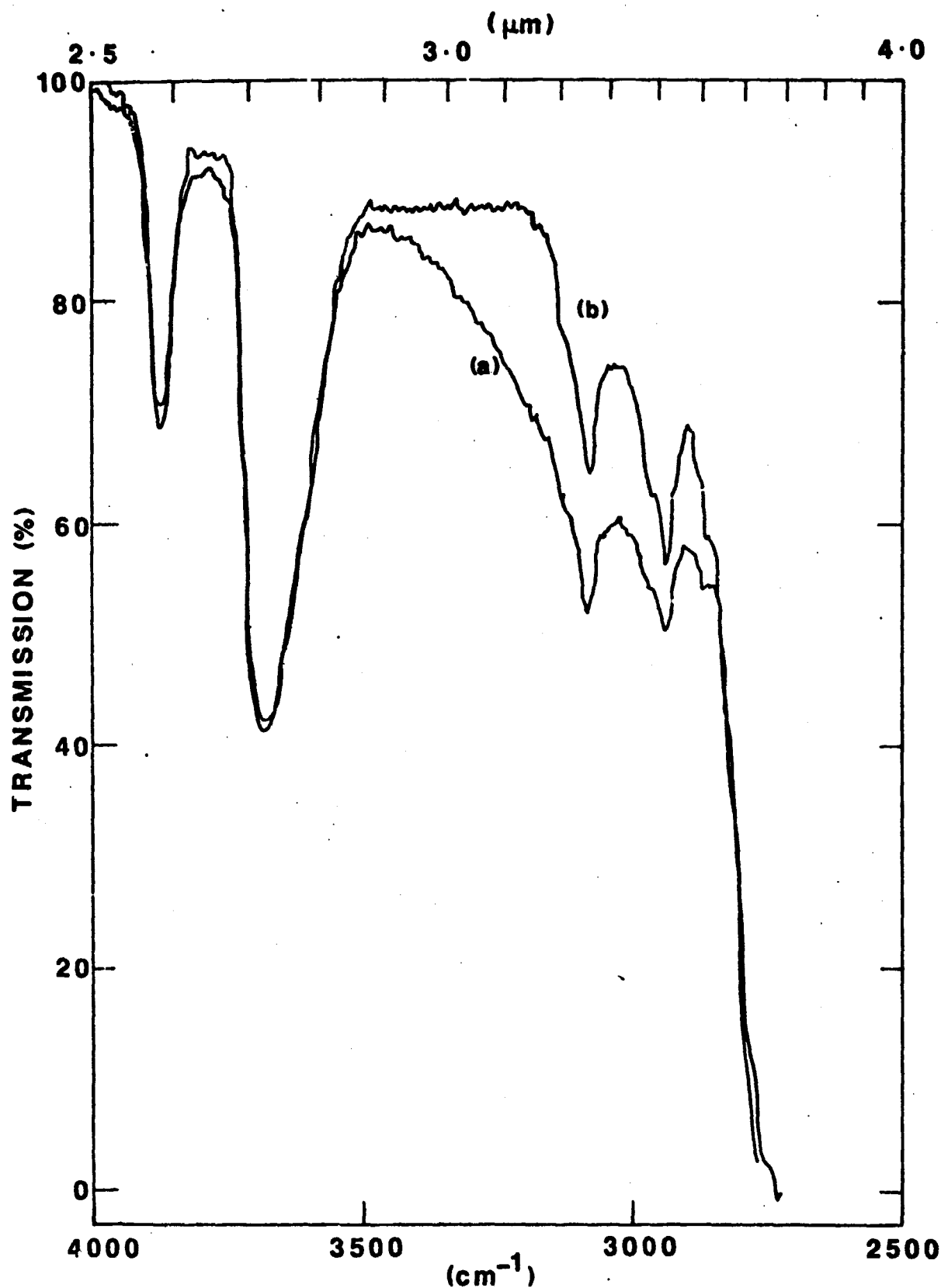


Figure 11: a) PoCl_3 distilled from Li
b) PoCl_3 distilled from Li, after further reaction with Li

NOTE: The window material accounts for the peaks at 3680 cm^{-1}

the POCl_3 spectrum. However, this variation could be due to a shift in the shoulder of the very intense absorption around 2600 cm^{-1} . Therefore, we never were sure exactly what the IR spectrum of the pure solvent should look like. (We later found another reported spectrum of POCl_3 (3) which tended to confirm our results.)

When we attempted to dry the reagent grade solvent with Li metal, the typical IR spectrum that we obtained of the distilled POCl_3 (see Figure 11a) was not indicative of a "dry" (no water reaction products present) solvent. Even when such a solvent was further "dried" by adding Li to the IR cell and waiting 24 hours, the peaks at $3000 \pm 100\text{ cm}^{-1}$ were still present (see Figure 11b). If one allows for what appears to be some protic contamination still present under the peaks at $3000 \pm 100\text{ cm}^{-1}$ and for the grating change shift at 3130 cm^{-1} , the 3070 cm^{-1} peak appears normal, but the 2940 cm^{-1} peak is decidedly more intense than seen in our "good" spectrum (Figure 10a). Again, this is evidence that the 2940 cm^{-1} peak is not inherent to the POCl_3 spectrum. However, every sample that we distilled either clearly showed this peak or had a large protic peak at 3070 cm^{-1} which might have hidden the 2940 cm^{-1} peak. So, inherent or not, once the peak was present we were not able to remove it by distillation.

2. The Laser Solution

In our second attempt after beginning to employ IR spectroscopy (July, 1982) we prepared a liquid which lased (October, 1982). The GTE people reported two different lifetimes, of $280\text{ }\mu\text{sec}$ and $340\text{ }\mu\text{sec}$, for this solution in the same paper (2). Therefore, depending on your choice of values, this preparation either did not meet (2, p 1372), met (1, p 1373), or exceeded (4) specifications for the laser solution, having a $t_{1/2} = 280\text{ }\mu\text{sec}$ and an approximate threshold energy of 70 J (with a 60% output coupler). Since the IR spec-

trum of the solvent contained additional peaks compared to the published spectrum, it is not surprising that we also observed these peaks at $3000 \pm 100 \text{ cm}^{-1}$ in our final laser solution (see Figure 12a). While our spectrum of the liquid in a 2 cm path length cell was better from $3500 \rightarrow 3150 \text{ cm}^{-1}$ (less absorption and flatter), we observed three distinct peaks, not seen in the published spectrum of the final solution, from $3150 \rightarrow 2900 \text{ cm}^{-1}$. The path length of the cell used in the published spectrum was not given, although it is believed to have been 1 cm based upon the intensities of other absorption bands. Therefore, the peaks between 3150 and 2900 cm^{-1} still should have been observable in the published spectrum, if the chemical species to which they correspond were present.

However, since we did make a good liquid which contained these non-removable peaks--whether indigenous or not--their presence seems not to have affected the performance of the liquid (July, 1982 preparation, Figure 12a). Therefore, whether they are inherent or not is probably of little concern. But, the inconsistencies between our spectra and the published spectra of both the "pure" solvent and the laser solution were a continuing problem for us throughout our work, i.e., we were never quite sure how pure our liquid was or which spectrum to believe or even whether it made a difference. It was only with some hesitation that we chose to compare all of our subsequent work to our own IR spectra, of both the solvent and final solution. (Later, we obtained another laser solution spectrum from GTE which was flat from 3500 3100 cm^{-1} and showed small peaks at 3040 and 2880 cm^{-1} .)

In our early work on this project we assumed that we could just follow a straightforward procedure without checking purity by IR at each step. We knew that we had made the solution once with a solvent which may not have been completely dry and tried to repeat that effort. However, since our first

(μm)

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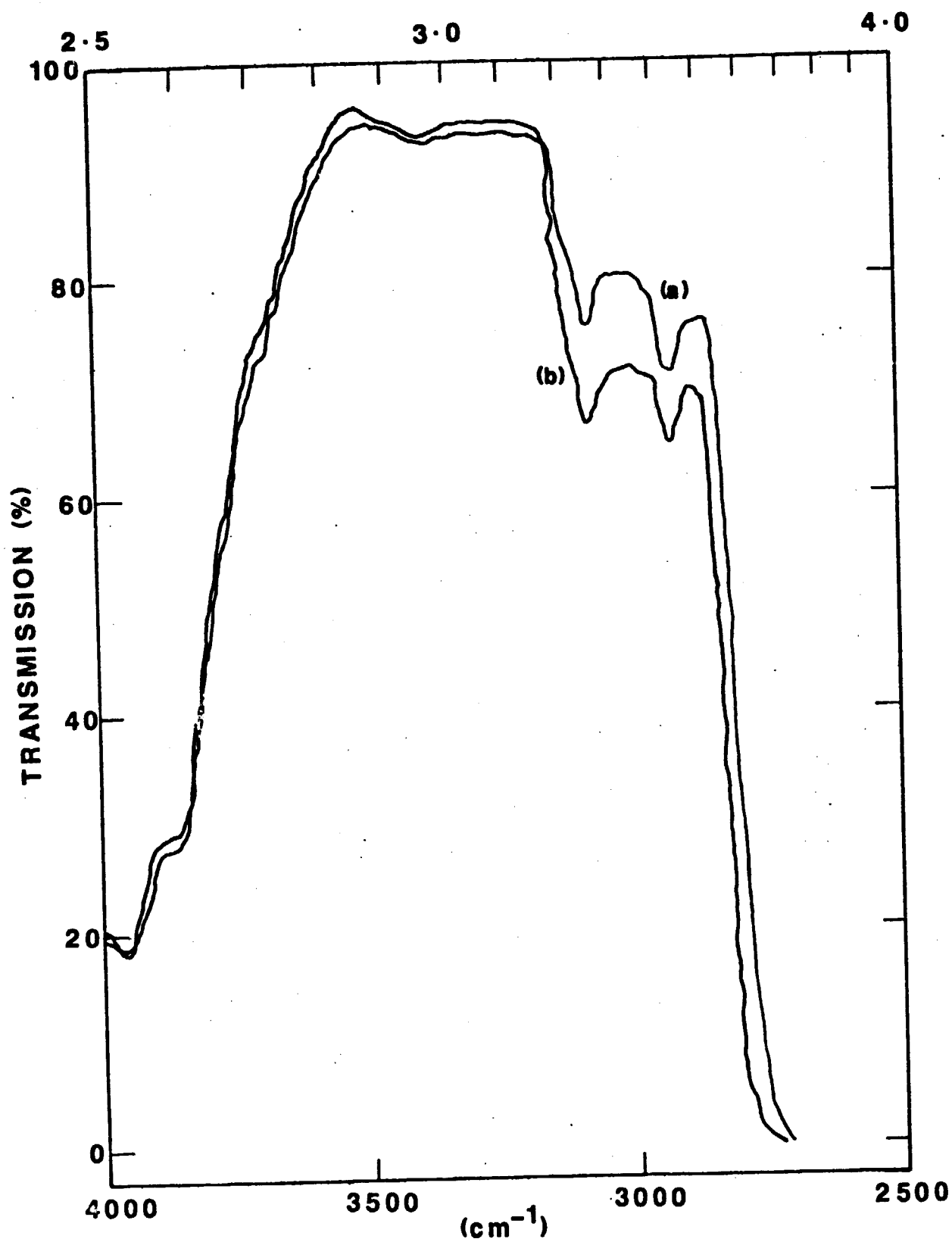


Figure 12: a) Laser Solution When Prepared
b) Same Sample, One Month Later

"successful" preparation of the lasing solution, all subsequent preparations have yielded solutions with lifetimes of only 140-150 sec. Clearly, the conditions for our procedure were not sufficient to allow us to prepare the solution routinely. This was the reason for going back and attempting to check the preparation in more detail. We obtained short lifetimes even when we did not observe any differences which were chemically significant in the IR spectrum of a given preparation compared to our "standard" IR spectrum (see Figure 12), i.e., when the only difference appeared to be the magnitude of the grating change absorption shift at 3130 cm^{-1} (vida supra). Based upon these spectra alone, neither we nor the people at GTE could explain the poor performance of the laser solution. We were therefore forced to conclude that IR analysis may not be sufficient to determine the quality of a given laser solution. If this is true, then an identification of the species causing the problem and a method of detecting it are still needed. However, alternate explanations were also considered (vida infra).

When the IR contained additional peaks it was clear that impurities were present and therefore they might explain the poor results. Again, this was additional evidence that our procedures were not adequate to protect the solution. However, the source and, therefore, the remedies for these impurities were not always evident, since peak assignments in the region $4000 \rightarrow 2500\text{ cm}^{-1}$ had not been made, i.e., the correlation between a particular IR peak and the chemical species responsible for that peak had not been made. It would seem that some of the "magic" needs to be removed from the procedure for preparing the laser solution, i.e., the events occurring in the solution need to be more clearly correlated with the manipulations of the solution. This will be possible only after some basic questions about the solution are answered by someone who can guarantee anhydrous conditions.

We have made some attempt to assign the peaks but these assignments are incomplete and very tentative. At the present time we cannot exclude the possibility of water contributing to any observed IR peak. There is definitely a need for additional work with better equipment to obtain exact answers. Therefore, since our IR assignments are tentative they should be used only as a guide.

Our beliefs regarding the IR spectra of the solvent and the laser solution, both before distillation to half volume and the final laser solution itself are summarized in the following Table I. All values given should be considered accurate to $\pm 10 \text{ cm}^{-1}$ and the following notations are used to indicate peak strength: weak (w), medium (m), strong (s), shoulder (sh), and broad (b). The $\text{Nd}(\text{TFA})_3$ was run in the solid phase (KBr pellet). The other spectra were run in 2 cm long cells.

Table I
Peak Assignments

| Peak # | Assignment | Components | | Laser Solution | |
|--------|---------------------------|--------------------------------------|-----------------|----------------|----------|
| | | $\text{Nd}(\text{CF}_3\text{COO})_3$ | POCl_3 | Before Distill | Final |
| 1 | | | | 3950(s) | 3950(s) |
| 2 | 2nd Overtone P=O | | 3860(m) | 3860(sh) | 3860(sh) |
| 3 | H_2O (?) | 3620(sh) | | 3620(sh) | |
| 4 | $\text{CF}_3\text{COO-H}$ | | | 3560(s) | |
| 5 | 1st Overtone C=O | 3420(s,b) | | | |
| 6 | | 3200(sh) | | | |
| 7 | | | 3070(w) | | 3070(w) |
| 8 | PC-H | | | 3070(s,b) | |
| 9 | | | | | 2960(w) |
| 10 | | | 2930(w) | | 2920(w) |
| 11 | 1st Overtone P=O | | 2600(s) | 2600(s) | 2600(s) |

Although peaks due to "free" water are seen as an impurity in the spectrum of POCl_3 at 3640 and 3560 cm^{-1} (see Figure 9b), we do not believe that the peaks seen in the laser solution before distillation at 3620 and 3560 cm^{-1} (peaks #3 and #4) are due solely to "free" water (see Figure 13). For one thing, the relative intensities are different and furthermore, we do not believe that an amount of water to which these peaks would correspond could be compatible with the solvent system, i.e., there would be too much "free" water. The fact that neither peaks #7 nor #9 are seen in the laser solution prior to distillation is due to the very intense #8 peak which completely dominates this portion of the spectrum.

This section is concerned with the problem of laser solutions which gave IR spectra yet had poor lasing quality. According to the people at GTE the only impurity that can explain the short lifetime is water (or more precisely, water reaction products) which they determine by the absorption at 3200 cm^{-1} . However, we believe that the absorption at 3000 cm^{-1} is a better gauge because there can be water contamination which will show up at 3000 cm^{-1} but not at 3200 cm^{-1} . We chose the value 3000 cm^{-1} because it is closer to the maximum absorption of PO-H (at 3070 cm^{-1}), yet the other small peaks in this region don't interfere at 3000 cm^{-1} . Figure 12a (compared to 12b) shows the effects of additional water contamination when an IR cell was not adequately sealed--there is increased absorption at 3000 cm^{-1} while the absorption at 3200 cm^{-1} is unaffected. This increased absorption could be possible because the limits of the self-cleaning reaction (vida infra) were overcome. We believe that the solvent or laser solution is "dry" when the absorption at 3000 cm^{-1} returns to within a few percent of the baseline, established between 3300 and 3200 cm^{-1} (after correcting for the grating shift).

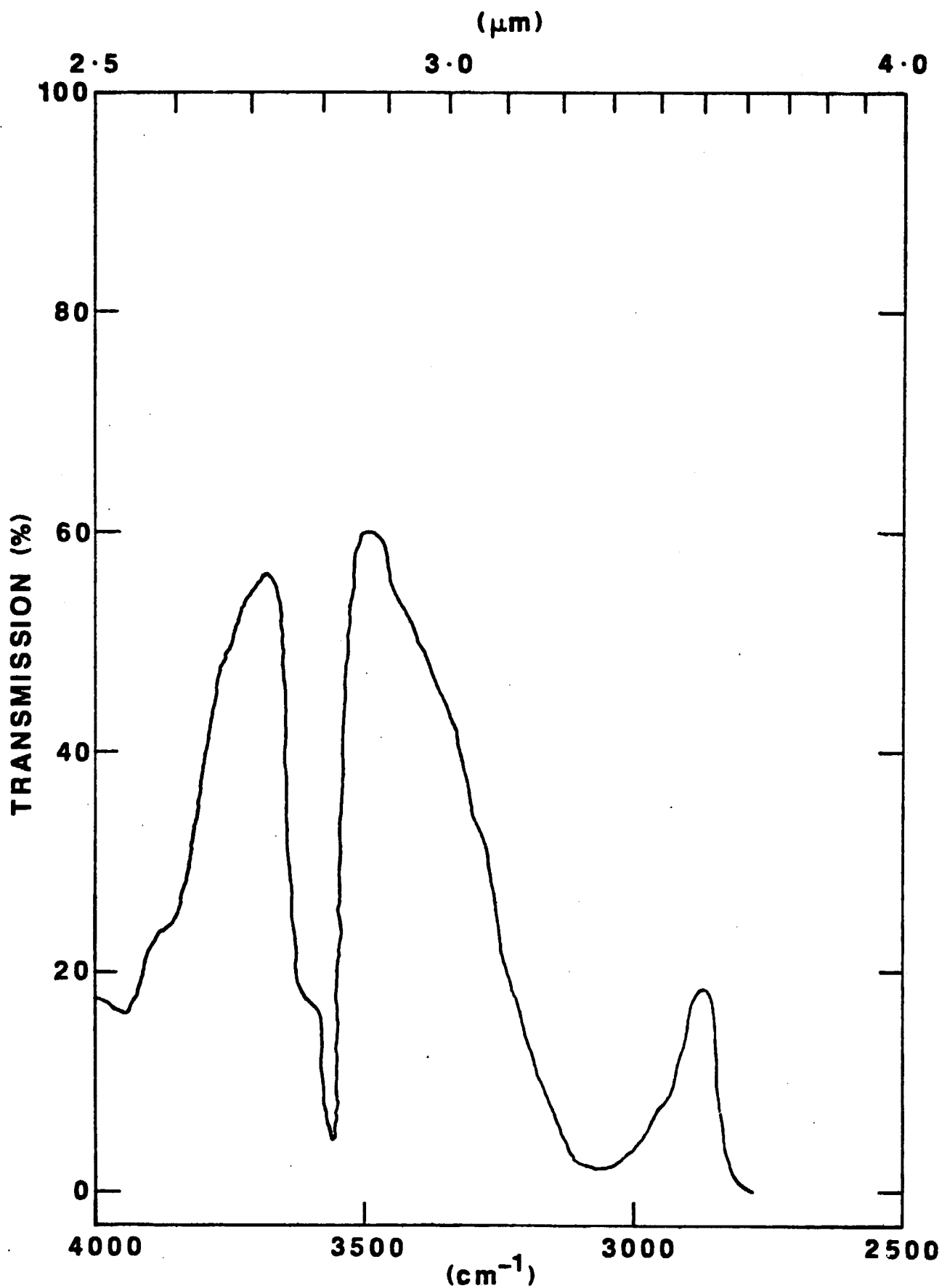


Figure 13: Spectrum of a Typical Laser Solution before Distillation to Half Volume

However, GTE also reports (2, p 1374) that deliberately adding water to the laser liquid only temporarily affects the liquid, i.e., the protic species ultimately reacts with ZrCl_4 to produce a precipitate, ZrOCl_2 , and HCl gas. It is claimed that careful filtration at this stage yields "...as good a laser solution as before [the water was added]." Therefore, if water is the problem why doesn't our poor laser solution with a short lifetime (if properly sealed) eventually precipitate ZrOCl_2 , liberate HCl , and become a good laser solution with a longer lifetime? The possible explanations include:

1. The presence of other impurities besides those resulting from water which lowered the lifetime,
2. The initial presence of too much water which results in either
 - (a) the loss of enough ZrCl_4 as ZrOCl_2 to substantially lower the lifetime (2, p 1372) (i.e., there is a limit to the self-cleaning which may have been exceeded), or
 - (b) the formation of certain known species containing the ZrO-H group which might be soluble in the medium and thereby maintain contamination in the solution.
3. Contamination by water which may have occurred during the filling of the laser cell (while at the same time occurred only infrequently when filling the IR cells).

An elaboration and explanation of these points follows.

We have not been able to show to our own satisfaction that the IR peaks in the region $3000 \pm 100 \text{ cm}^{-1}$ are inherent to the spectrum of the "pure" solvent and the final laser solution. Based upon their variation in intensity from run to run, these peaks are either not characteristic or there is a broader peak which is not characteristic and lies under these characteristic peaks which increases their intensity. Either way there is some impurity present which may

very likely be protic. Also, there exists the possibility that certain small peaks lie under the very intense peaks which are present in the spectrum and are therefore undetectable.

We believe the process of self-cleaning of the laser solution works on a small scale. However, adding large amounts of water would result in removal of large amounts of ZrCl_4 from the solution. Figure 7 in reference 2 shows how this would decrease the lifetime. It is difficult to believe that the amounts of precipitate that we were seeing corresponded to gram quantities of ZrOCl_2 . If large amounts were precipitating, then clearly the conditions were not sufficiently dry.

It is also possible that some of the ZrCl_4 which had reacted in the solution was very tightly bound and could not react to form ZrOCl_2 . However, there would still be Zr-Cl bonds available to react with various protic species present in the solution and in doing so form Zr-OH bonds. If these Zr-OH containing species were soluble in the medium then the protic contamination would remain in the liquid. Therefore, there is a need to determine the limit to which water can be added to the laser liquid and still have a good laser solution.

The third point, the apparent inconsistency with encountering problems in transferring the solution, might be resolved by realizing that our procedure for transferring the solution to a laser cell is more complicated than transferring it to an IR cell. Therefore, the additional manipulations required (with only the minimal protection of a glove bag) would provide more of an opportunity for contamination to occur. But, our solution transfer problems seem to be random, sometimes resulting in precipitation in filling the IR cells.

Another aspect of the solution chemistry which needs to be examined involves the final step. Since distillation to half volume was supposed to remove protic contamination, the question becomes what was the protic species being distilled? It would seem that adding small amounts of water to $\text{POCl}_3/\text{ZrCl}_4$ can only generate HCl gas and either HPO_2Cl_2 or ZrOCl_2 , respectively. (Supposedly any HPO_2Cl_2 would be converted to POCl_3 by ZrCl_4 and form ZrOCl_2 .) It is not clear exactly what the fate of any protic species is from this point on, i.e., what function does distilling the solution have? Would just heating (refluxing) the solution accomplish the same thing, as might be the case if HPO_2Cl_2 broke down into HCl gas and $\text{P}_2\text{O}_3\text{Cl}_4$? If CF_3COOH is distilling, it should distill easily but, removal of some TFA in this manner may partially prevent formation of PO_2Cl_2^- ($\text{CF}_3\text{COO}^- + \text{POCl}_3 \rightarrow \text{CF}_3\text{COCl} + \text{PO}_2\text{Cl}_2^-$) which is needed to complex the neodymium ion in solution. On the other hand, if one is actually distilling a hydroxy derivative of POCl_3 then it may be necessary to significantly reduce the volume until little unreacted solvent is left and the boiling point of the remaining viscous liquid increases to the point where the protic species will distill. Some basic chemistry needs to be done on the effects of adding small amounts of water to POCl_3 and heating (especially, in the presence of TFA salts).

B. Recommendations

The following section contains some specific recommendations for modifying the procedure to improve the consistency of the preparation. For all of the modifications and possible improvements of our previously reported (see March 1983 report) procedures that we are suggesting in this section, we are not aware of any significant differences between our conditions for the preparation of the solution with a long lifetime relative to those with short lifetimes. We believe that the procedures outlined previously, although not foolproof, are

generally adequate with some additional essential equipment. This equipment includes: additional IR cells to be able to monitor the solution contents more often throughout the preparation, an inert atmosphere box to protect the various manipulations and transfers of the solution and its components and to store the final solution, and enough hood space to set up all necessary apparatus at the same time. The changes are listed by using the section headings from the original report to which the suggestions apply.

- C. Although our $\text{Nd}(\text{TFA})_3$ was heated to a constant weight which our calculations indicated was anhydrous, we were afraid of decomposing the solid if it was allowed to get too hot. Therefore, we suggest that thermogravimetric analysis be run on a sample of $\text{Nd}(\text{TFA})_3$ to check its purity and determine to what temperature the solid can safely be heated for prolonged periods of time. This will allow a correlation between the IR spectrum and purity to be made.
- D. We could not keep POCl_3 dry in the distillation apparatus for an extended period of time. This implies that the system leaks. This problem might be solved by the use of a more standard still which did not have stopcocks and also the use of Teflon tape at all joints. If we had a better way to store the solvent (i.e., in an inert atmosphere) there would not be a need to try to use the still for this purpose. Also, rinsing all glassware with alcohol and drying in a vacuum oven would allow for quicker assembly of the cooler glass.
- F. Don't assume anything about the standard conditions for distilling the solvent. After treating the solvent with Li for 24 hours, sample the solvent before distillation and sample each fraction of distillate to insure dryness at each step.

- G. All operations should be done in a controlled atmosphere box with an antechamber, rather than in a glove bag. If the IR of the final solution is still "wet" the distillation to half volume should be repeated. Also, one should consider the possibility of adding excess ZrCl_4 to "dry" the solution.
- H. All glassware (especially, the laser cell) that comes into contact with the final laser solution should be rinsed with dry POCl_3 before filling with the laser solution. Contrary to both the March 1983 and June 1983 reports, we now believe that the best method to attach the windows to the body of the laser cell is with a fuseable ceramic tape.

The overall procedure may not require these ultra-dry conditions but these conditions will be necessary to troubleshoot the problems we were having with the preparation. Additional equipment is definitely needed in order to make the interpretation of future results meaningful.

C. Spectral Properties - Electronic

Absorption spectra of the laser liquid can be used to determine if a sufficient concentration of the Nd^{3+} ion has been obtained in the solution. There are 5 absorption bands of the Nd^{3+} ion in the spectral region between 500 and 900 nm. As can be seen in Figure 14, the absorption bands are present in sufficient intensity. The results shown indicate that the solution contains approximately 1 0.3 molar concentration of Nd^{3+} ion. The spectra is obtained using a Tracor Northern (TN-1710) Optical Multichannel Analyzer attached to a 1/4 meter Jobin-Yvon grating spectrometer. The light source used was a calibrated tungsten ribbon lamp. The absorption cells used were Beckman 20 mm cells with Near IR silica windows.

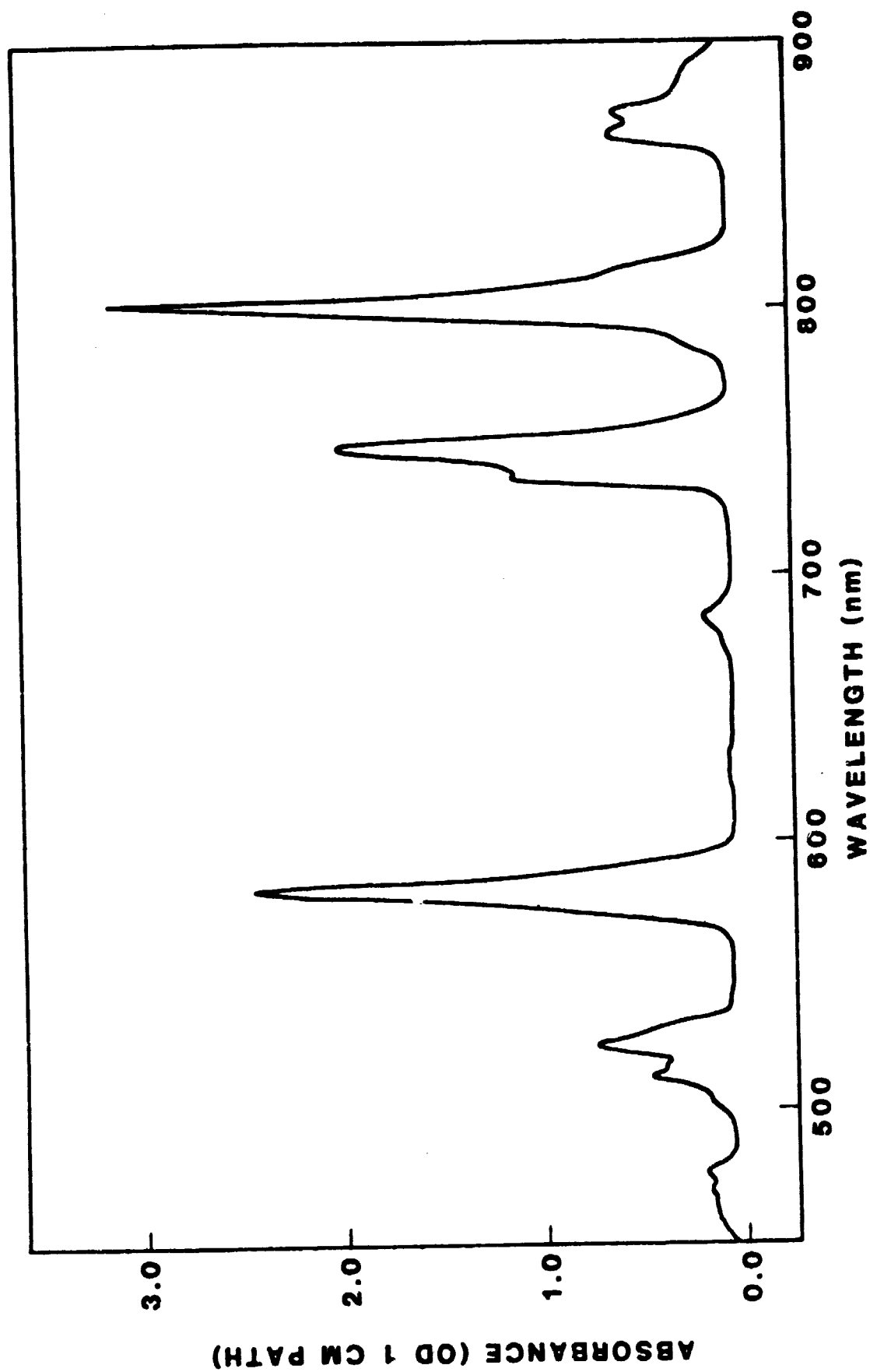


Figure 14: Electronic Absorption Spectrum of the Laser Solution

D. Lifetime Measurement

Perhaps the most sensitive parameter regarding the quality of the laser liquid is the Ncl^{3+} upper state lifetime. Values reported in the literature for the optimum lifetime vary between 280 and 340 μsec . The experimental set-up for measuring lifetime is shown in Figure 15. Lifetime measurements are made in the laser cells. As shown there are two photodiodes used. One observes the flashlamp excitation pulse and the other observes the fluorescence decay from the liquid through a $1.05 \mu\text{m}$ interference filter. Typical data are shown in Figure 16. The lifetime is measured by the observed time it takes the intensity of the fluorescence to decay a factor of $1/e$. The data is taken after the flashlamp pulse has returned to baseline to avoid any convolutions with the pump pulse.

V. LASER PERFORMANCE PARAMETERS

A. Measurement of Small Signal Gain at $1.05 \mu\text{m}$

To measure small signal gain, the following procedure was used. The liquid is transferred to a quartz cell and placed in a flashlamp housing which contains two EGG FX-81-C-8 flashtubes. The flashtubes are energized by 7 capacitors (200 Joules each) in parallel. They are triggered by a pulsed 30 kV high voltage source. The flashlamp housing is placed on an optical bench in line with a 500 mW CW Nd^{3+} :YAG laser. The YAG probe beam passes through the liquid cell and is detected by a PIN photo diode. A $1.05 \mu\text{m}$ interference filter is placed in front of the photo diode for discrimination against other wavelength light. (See Fig. 17). The gain measurements are made as follows:

1. The flashlamps are fired with the probe beam off. The fluorescence intensity of the Nd^{3+} is measured. ($1.06 \mu\text{m}$ only).

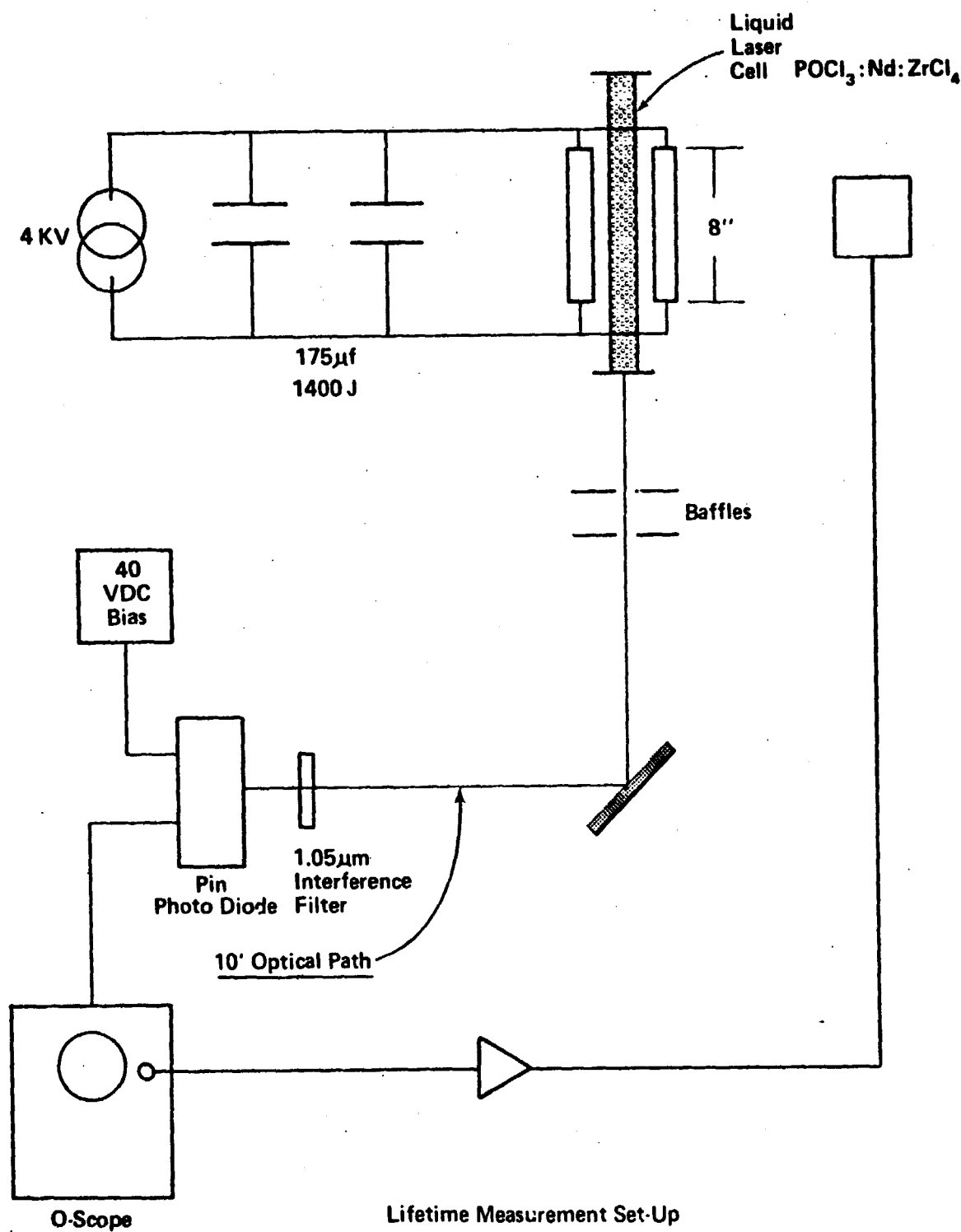
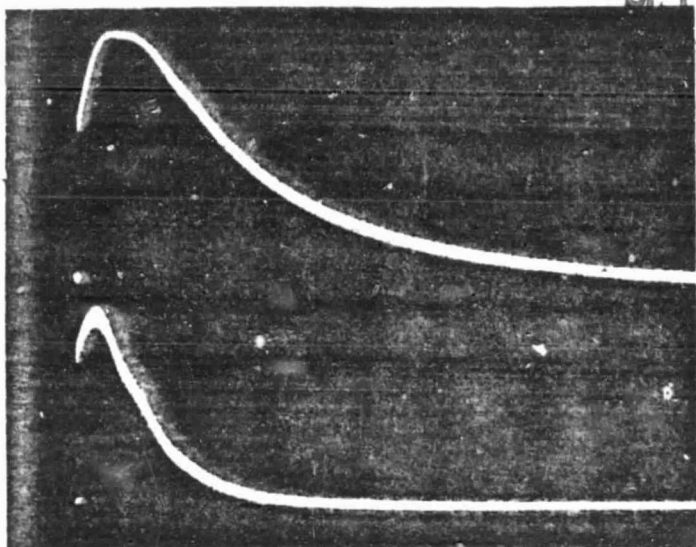


Figure 15.

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OF POOR QUALITY



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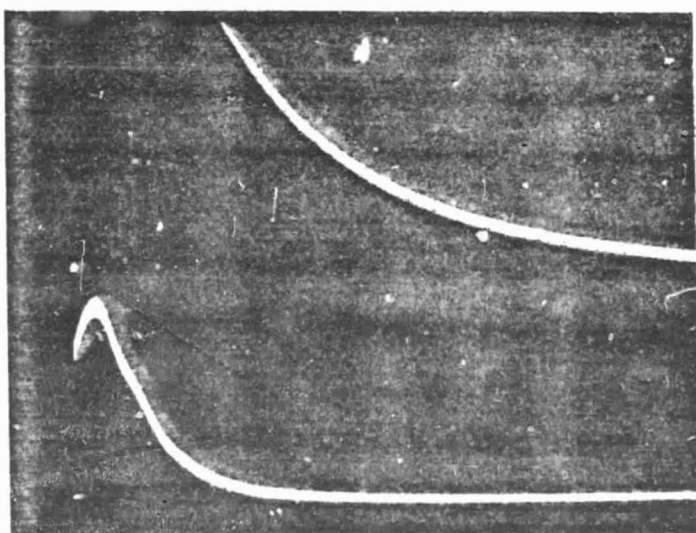
1.05 μm Florescence

2V/cm 50 $\mu\text{s}/\text{cm}$

Lower Trace:

Flashlamp (all Wavelengths)

20V/cm 50 $\mu\text{s}/\text{cm}$



Upper Trace:

1.05 μm Florescence

1V/cm 50 $\mu\text{s}/\text{cm}$

Lower Trace:

Flashlamp (all Wavelengths)

20V/cm 50 $\mu\text{s}/\text{cm}$

Figure 16 : Lifetime Measurement Data

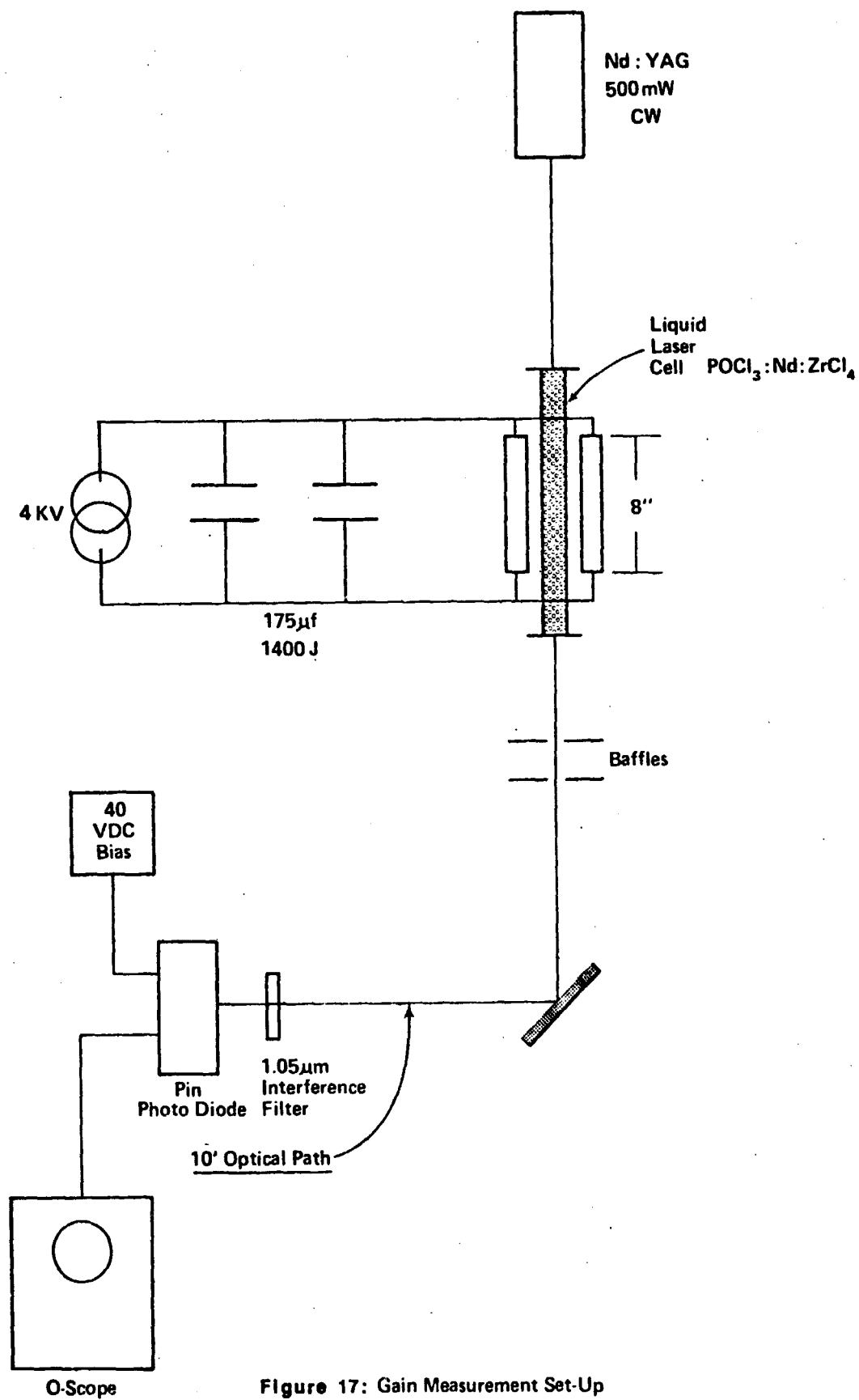


Figure 17: Gain Measurement Set-Up

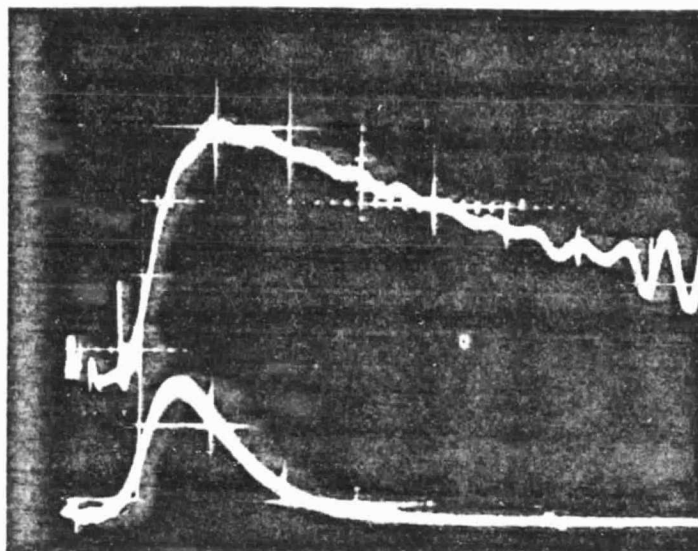
2. The same procedure is repeated with the probe beam on. The YAG probe beam produces an intensity output of about 10 volts in absence of flashlamp pumping. During the gain shots the intensity of the output beam is increased to about 24 volts, thus indicating a gain of about 2.4 (see Fig. 18a). Note that in 18b the gain is much lower and the pulse actually returns below the baseline. In this case, the liquid was still warm from the previous shot and gain was produced only during the pump pulse (50 μ sFWHM) and afterwards the liquid began to absorb the probe beam.

In the first shot - using a cool liquid - the gain lasts much longer, about 200 μ s as can be seen in Figure 18a. This compares to the upper state lifetime of the Nd^{3+} of about 330 μ sec. Therefore, the liquid produces gain until the upper state has been drained. For time comparison, Figure 18b also shows the flashlamp pump pulse taken perpendicular to the gain axis (all wavelengths). The flashlamp emission indeed ceases before the gain goes to zero.

B. Lasing of the $\text{POCl}_3:\text{Nd}^{3+}:\text{ZrCl}_4$ Liquid by Xenon Flashlamp Pumping

The experimental set-up for the lasing attempts was similar to the gain measurement set-up with the exception of the probe laser and the addition of cavity mirrors as shown in Figure 19. The energy storage capacitor (7 25 μ f capacitors @ 4kV) was connected to two EGG FX-81-C-8 Xe Flashlamps in parallel. They are fired by a 30 kV trigger pulse. The laser cavity consists of a 30 ml volume of the liquid 12" (30.5 cm) cavity length in a hemispherical cavity consisting of a flat 1" (2.54 cm) dia. 99.9% reflecting mirror and 2 m radius 60% reflecting output coupler. The laser output pulse is reflected off of a 99.9% reflecting mirror (at 1.06 μ m) blazed at 45° and focused (quartz lens) on a PIN Photodiode behind a 1.05 μ m interference filter. The flashlamp output is also monitored by a PIN DIODE. Both diode outputs are monitored by a 555 Tektronics Oscilloscope.

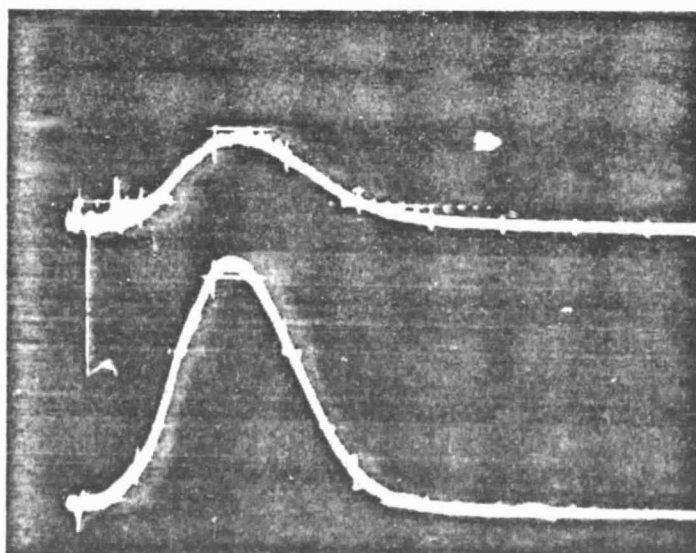
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gain (cold liquid)

Upper Trace:
gain profile
 $50 \mu\text{s}/\text{cm}$ time base
5V/cm
(probe input 5V)

Lower Trace:
Flashlamp Output



gain (hot liquid)

Upper Trace:
gain profile
 $50 \mu\text{s}/\text{cm}$ time base
2V/cm
(probe input 5V)

Lower Trace:
Flashlamp Output

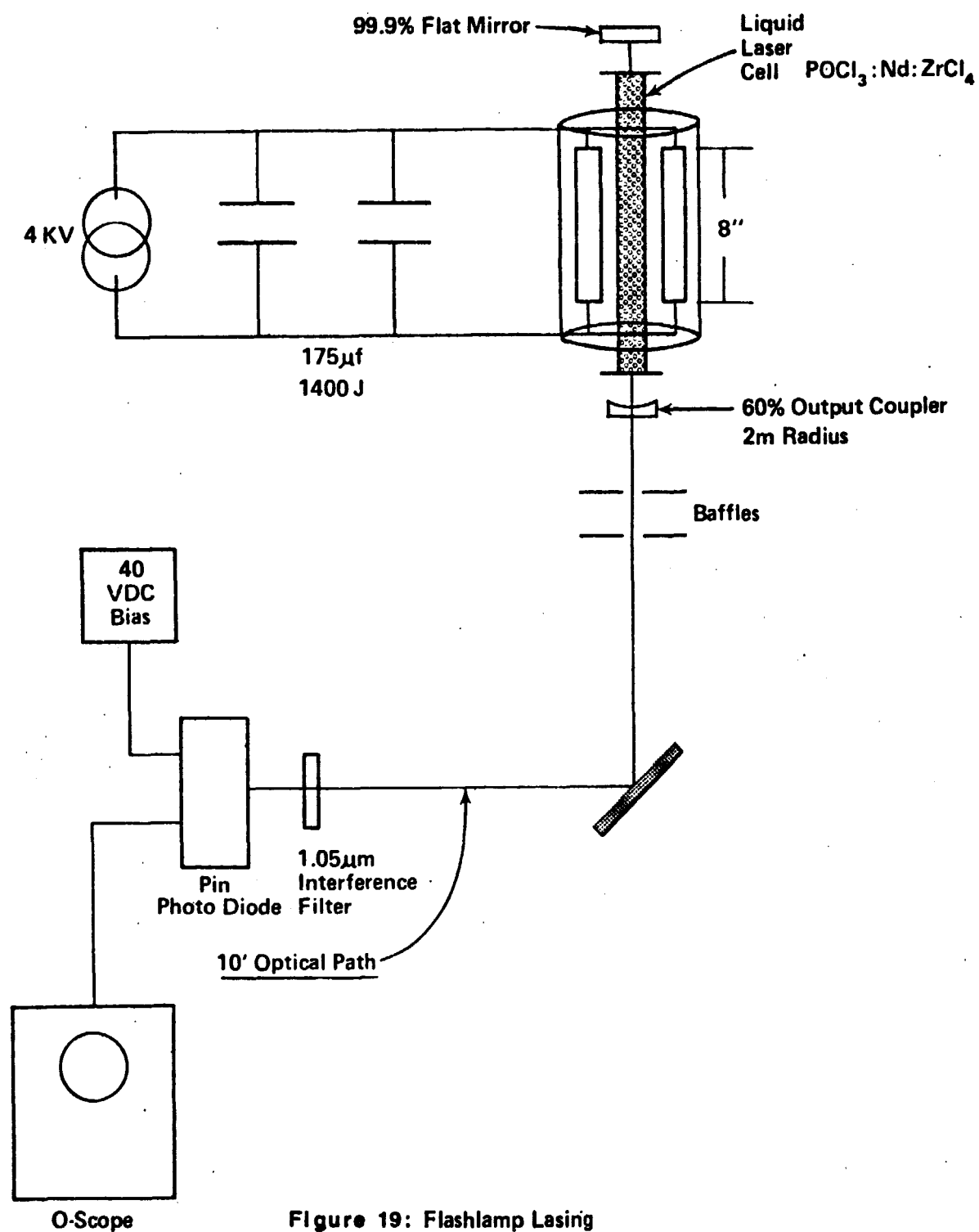
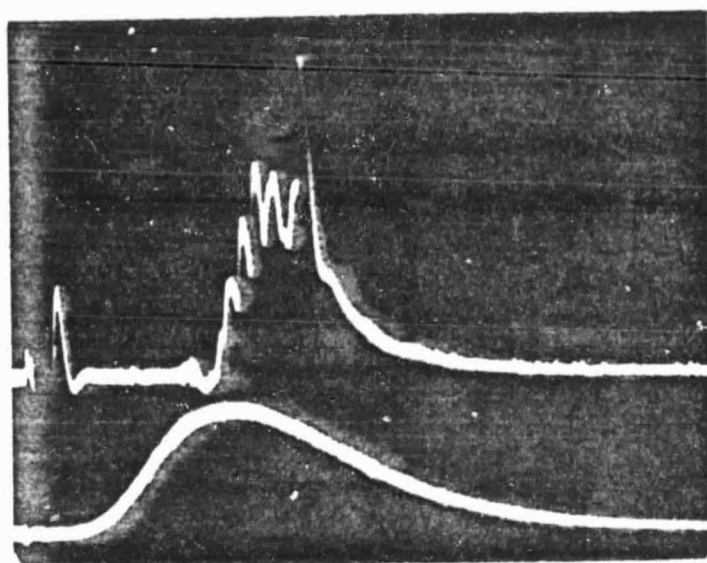


Figure 19: Flashlamp Lasing

Figure 20 shows the laser and flashlamp output. The time base is 20 μ s/cm. As shown the laser output is delayed from the onset of flashlamp excitation by about 20 μ s and has the characteristic ringing of high gain lasing systems. The energy stored in the capacitors during this shot was 100J and the estimated laser output energy is about 2J.

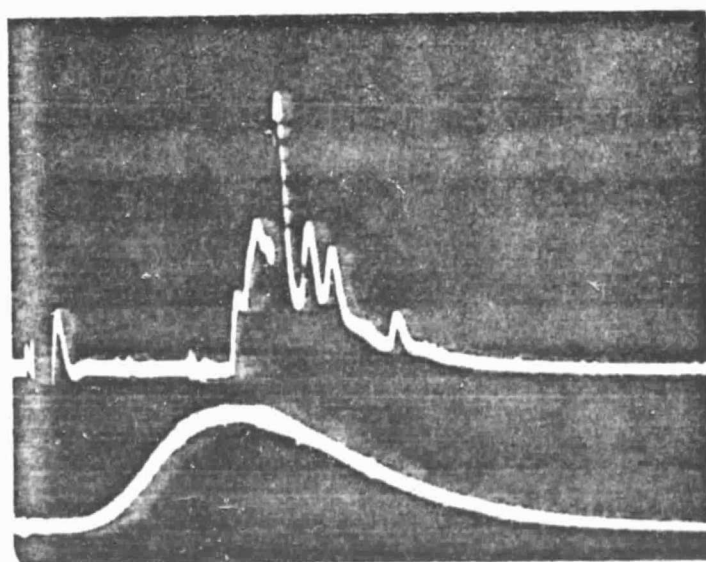
C. Minimum Pumping Power

In order to obtain the minimum values for the pumping power necessary for lasing, we made an effort to optimize all conditions, i.e., minimize all losses. The optical quality of the windows on the all Pyrex cavity described in Section II, H of the last Annual Report proved to be unsatisfactory. This was because the windows used were either not flat enough initially or were distorted as a result of fusing them onto the body of the laser cavity. (They were only 10 mm in diameter and heating them may have altered the optical quality at the center of the windows.) For expedience, an all quartz cavity with 1" diameter windows (flatness to 0.002") was fabricated. Both windows were fused onto the body of the laser tube so that they were approximately perpendicular to the tube axis. In a dark room, the laser tube was placed in a glass lathe and held firmly while a He/Ne laser beam was passed through the center of the tube. Then, in order to insure minimum losses, the alignment of one of the windows was optimized by heating the tube near that window until the quartz softened and adjusting the exact position of the window with respect to the tube until the reflected beam was in superposition with the incident beam. The tube was then reversed and the process repeated. This procedure, which minimized reflective losses, allowed us to use fused windows--instead of windows sealed onto the tube body with O-rings, as had been the practice of other researchers.



Upper Trace:
Laser output ($\sim 2\text{J}$)
 $20\text{ }\mu\text{s/cm}$

Lower Trace:
Flashlamp output ($\sim 100\text{J}$)
 $20\text{ }\mu\text{s/cm}$



Upper Trace:
Laser Output ($\sim 1.4\text{J}$)
 $20\text{ }\mu\text{s/cm}$

Lower Trace:
Flashlamp output ($\sim 80\text{J}$)
 $20\text{ }\mu\text{s/cm}$

Lasing of the $\text{POCL}_3:\text{Nd}^{3+}:\text{ZrCl}_4$ liquid by Xenon flashlamp pumping

Figure 20.

In order to better understand the lasing characteristics of the $\text{POCl}_3:\text{Nd}^{3+}:\text{ZrCl}_4$ liquid, several experiments were performed utilizing a Nd:YAG Rod. The performance of the YAG is well documented and very reproducible. The laser liquid on the other hand seems to have a very wide range of performance characteristics which at this point are not clearly understood. Nevertheless, by using the Nd:YAG as a "standard" reference, we were able to gain a better understanding of the liquid.

To determine the minimum pumping power for the liquid, it is necessary to determine the threshold energy since we are operating in the pulsed mode. Several values for the threshold energy are reported in the literature.^{2,3,4} Figure 21 shows a plot of the threshold energy vs output coupling ($\ln R$) of the $\text{POCl}_3:\text{Nd}^{3+}:\text{ZrCl}_4$ liquid measured by us, several referenced values, and the Nd:YAG for comparison. As shown, the threshold energy measured varies between 65J and 110J whereas the Nd:YAG threshold is approximately 0.5J. The actual threshold energy measurements were performed as follows: the liquid (or YAG) cell was placed and aligned in the cavity described in the previous report. The laser was fired at different energies for various output couplers (i.e., 98, 95, 80, and 60%). The output energy produced from each input energy (and output coupler) was measured by a digital energy meter (calorimeter). A plot (shown in Figure 22) of the measured output energy vs input energy (measured as voltage across the storage capacitors) for each output coupler was then made, producing a family of slopes which when extrapolated to zero output energy yields the threshold energy for each output coupler. A similar set of data was collected for the Nd:YAG Rod (see Figure 23).

Previously the threshold energy of the liquid (of a previous batch) was measured by a crude technique (we did not have the energy meter then) which indicated that the threshold energy for the liquid (with a 60% output coupler)

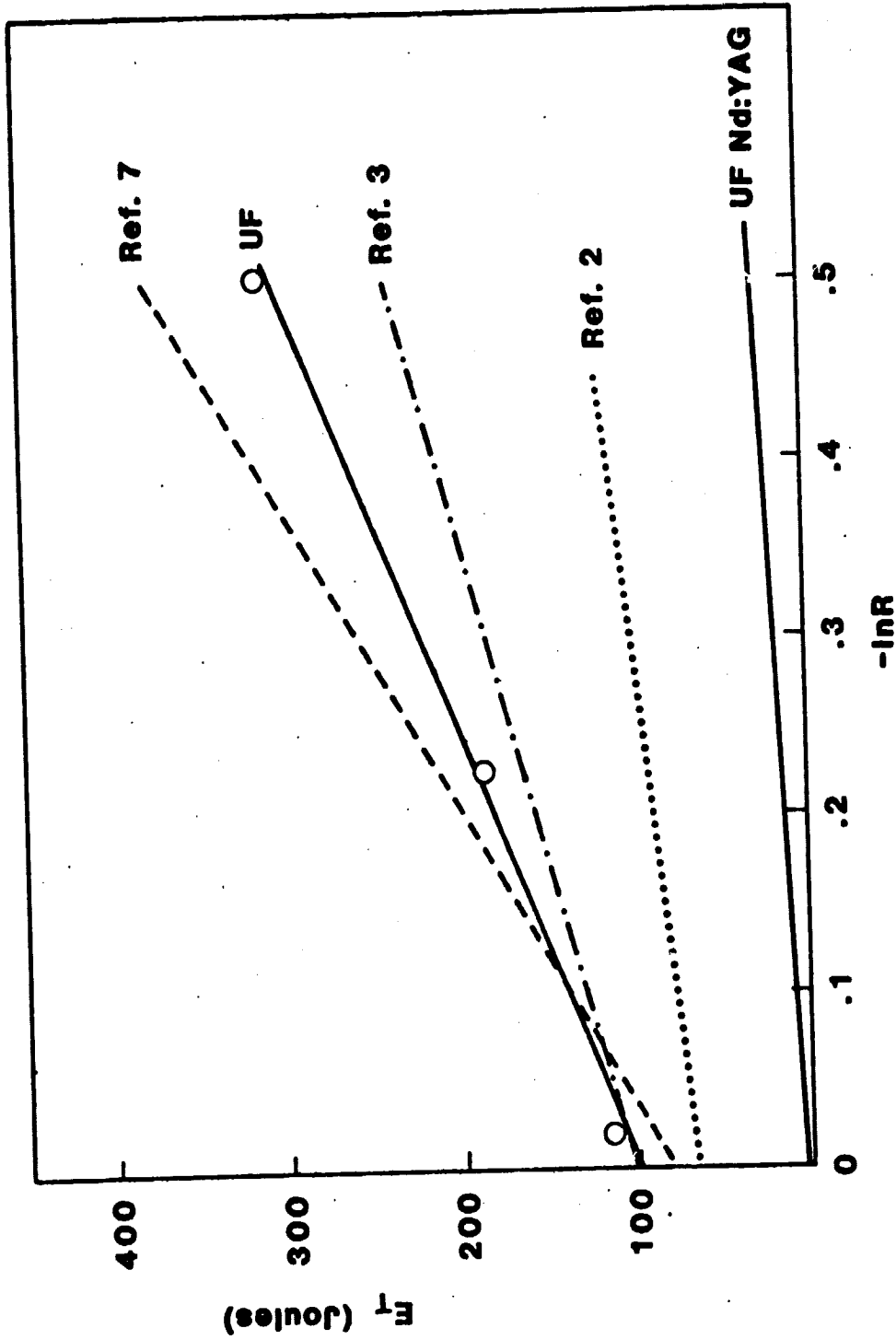


Figure 21: Threshold Energy vrs Output Coupling for the
POCl₃ : Nd : ZrCl₄ Liquid Laser Solution and YAG

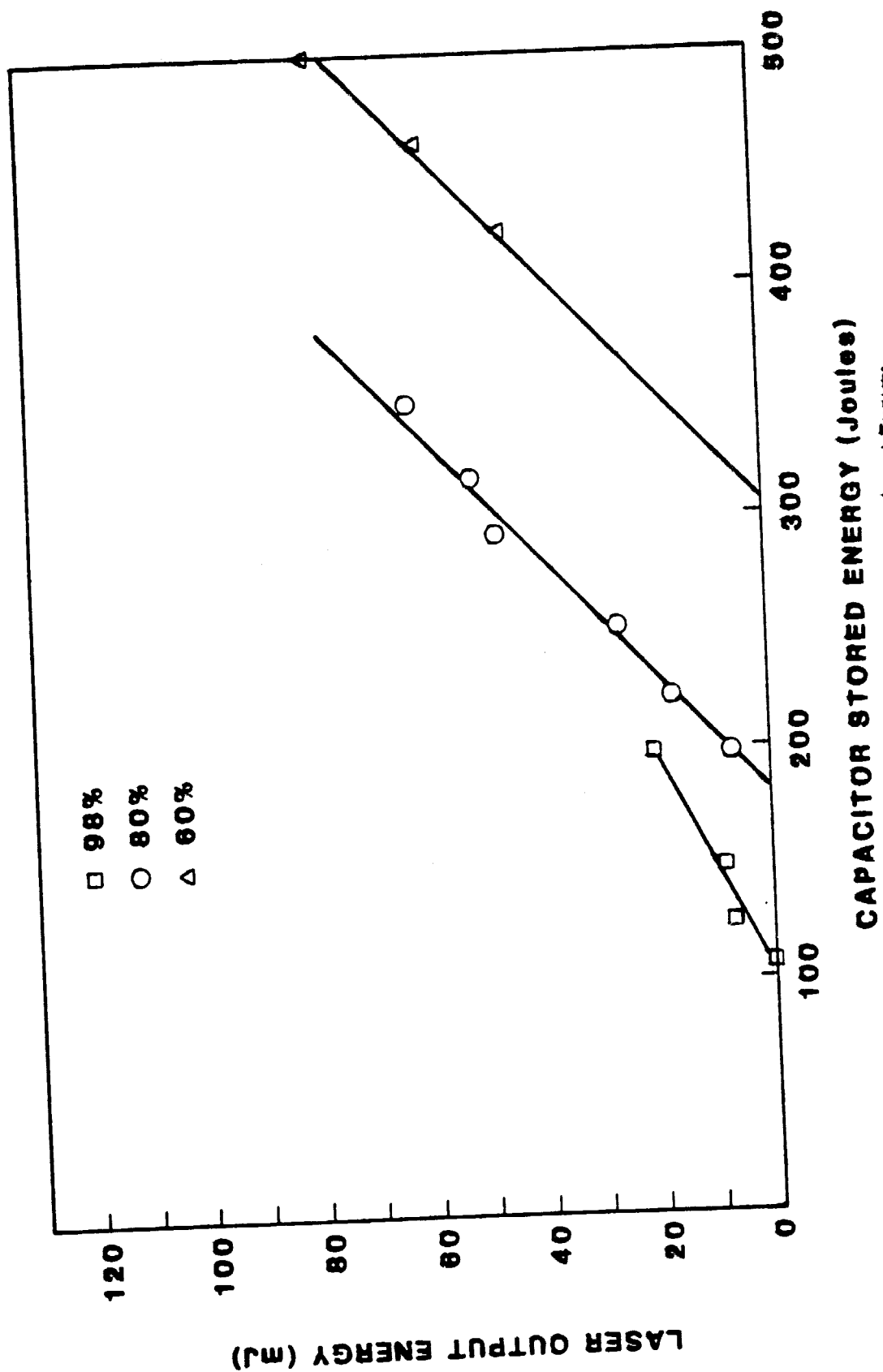


Figure 22: Laser Output Energy vs Input Energy
for Three Output Couplings

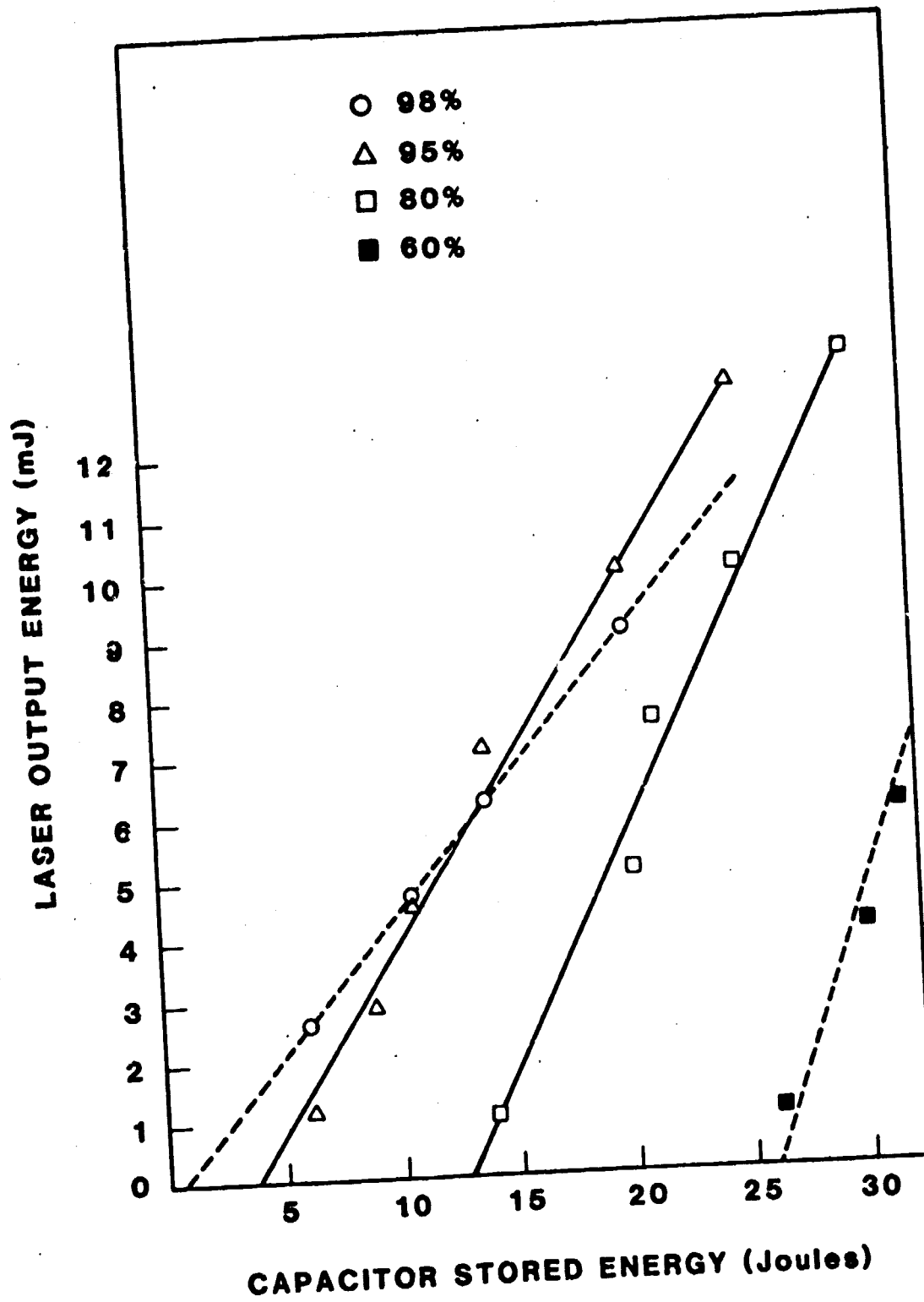


Figure 23: Laser Output Energy vrs
Input Energy for the Nd:YAG Laser

to be 70J. The technique used then was performed as follows: the liquid laser was fired at different energies and the laser output was monitored by a PIN diode and oscilloscope. Lasing action was verified by the characteristic spiking and vertical rise time on the recorded scope traces. The energy input was successively reduced until no lasing action was observed. This data point has not been reproducible in the successive liquid laser batches we have thus far produced. Unfortunately, the batch that produced the best results had to be scrapped due to contamination from a leaky cell. Although we have greatly improved our liquid laser cell technology, we have been unable to reproduce the liquid that yields as good a performance. The diagnostic scans of the liquid show very little difference in quality between the batches yet the performance from each batch varies quite a bit.

VI. SOLAR SIMULATOR EXPERIMENT

A. Introductory Remarks

The demonstration of solar pumping of a laser medium, has eventually to be done in the field using the sun as light source. While this seems to be straightforward, it turns out that the fact that one is outside an established laboratory exposed to the elements, that the weather is unpredictable, and that the sun moves rather fast, poses formidable problems.

One either has to have a solar facility, similar to an astronomical observatory, where the experiment can be kept inside a building, or one has to be at a stage of development where the experiment is already sufficiently ruggedized to put up with the adversities imposed by the elements.

Since in the present research program neither is the case, it seemed to be advisable to attempt lasing in a solar simulator first and continue after being successful with experimentation using the sun as a light source.

Lasing, using the sun as light source, has to be considered as the final demonstration of the concept, however, in the meanwhile, lasing in a solar simulator allows a somewhat broader approach for acquisition of data.

The solar simulator was limited to a shortest rise time of 1 millisecond. This is a rather long time, compared to the lifetime of the upper laser level. A measurement of threshold energy as a function of rise time should certainly include rise times shorter than the lifetime of the upper laser level. For this reason, the rise time measurements were made with flashlamps only.

B. Determination of Threshold Energy as a Function of Rise Time

While there is no good theoretical reason based on the energy level diagram of the liquid neodymium laser system which would state that this laser cannot operate CW, it seems that heating effects will eventually terminate lasing. The way around this would be to flow the liquid through the irradiated area. A certain slug of the liquid has to have a shorter residence time than is required for the heating effects to shut down laser action.

The entering of a certain slug of liquid into the irradiated area constitutes a certain rise time for irradiation. Therefore it is important to know if there is a relationship between rise time and threshold energy, since it determines the minimum fluid velocity for a given level of irradiation.

The following measurements were made (using two EG&G Flashlamps in parallel) by varying the voltage, ohmic resistance and capacity of the flashlamp power supply circuit.

Figure 24 shows a plot of required optical threshold energy versus rise time. As can be seen, the required threshold energy approaches a maximum when the rise time becomes larger or large compared to the lifetime of the upper laser level. (CW Lasing). In order to achieve low thresholds, the rise time should be small or at least smaller than the lifetime of the upper laser level.

Risetime vs. Threshold Energy

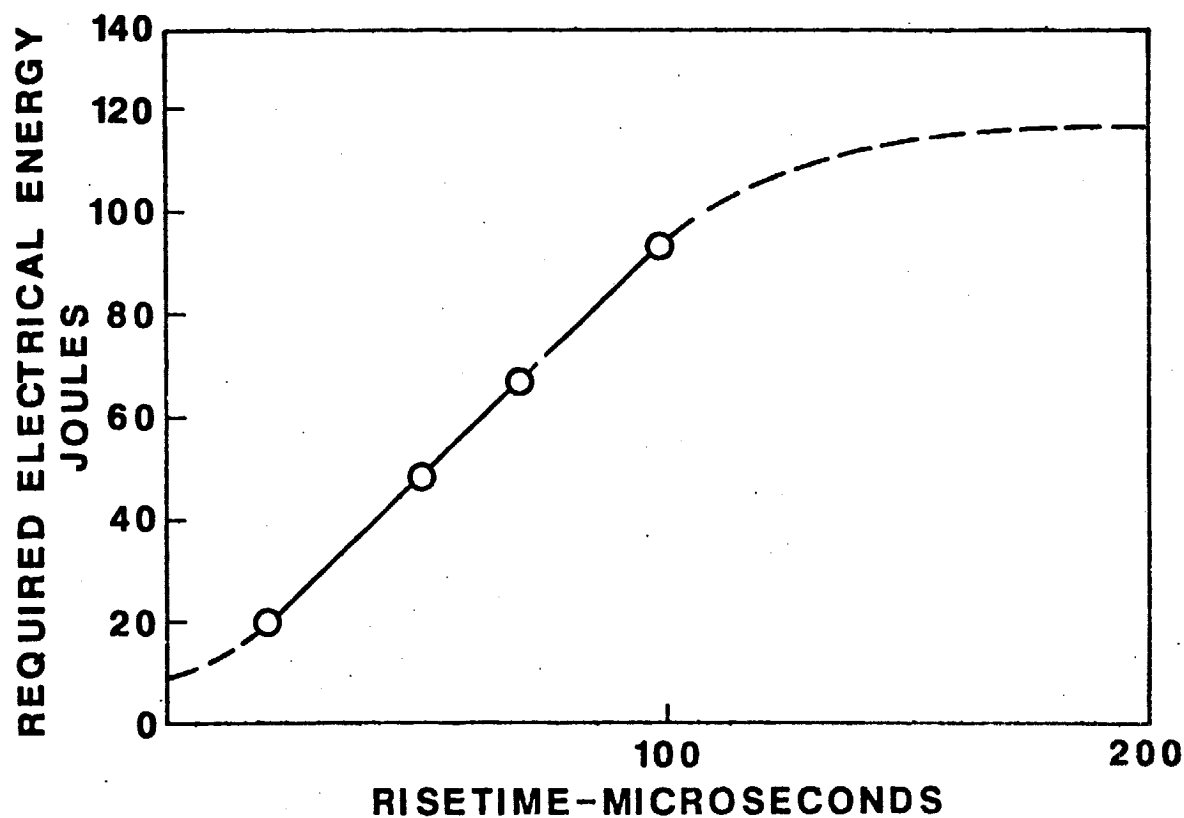


Figure 24.

A rise time of 20 μ sec is a desirable goal. While it is possible to build a shutter which would chop the available D.C. light into pulses having such a rise time, the solar simulator still could not provide sufficient light to pump the laser.

According to the information given to us, the solar simulator will deliver 4 KW (light) into the laser. Based on the results shown in Table II, one can conclude that the required power to overcome threshold is 10 KW (light) or less. It is certainly possible to improve the existing liquid somewhat, let's say by a factor of 2. It is also possible to reduce the cavity losses, maybe by a factor of 2, so that a maximum overall reduction of the required optical power by a factor of 4 could be expected.

Table II

| Rise Time (sec) | Required Electrical Energy (Joules) | Required Optical Energy (Millijoules) | Optical Energy the simulator would deliver (Millijoules) | Required Optical Power in KW |
|---------------------|---|---|---|------------------------------------|
| 20 | | 20 | 200 | 80 |
| 50 | | 49 | 490 | 200 |
| 100 | | 93 | 930 | 400 |
| 200 | | 120 | 1200 | 800 |

The required "optical power in" was estimated based on the solid angle subtended by the flashlamps. Losses due to reflection or refraction could only be speculated upon. It is, therefore, conceivable that the electro-optical coupling efficiency used in the calculations of 1% is considerably in error, maybe as much as a factor of 4. Consequently, based on the above measurements, it is not inconceivable that an overall improvement of one order of magnitude may be required in order to lase with the solar simulator alone. However, the following section of this report suggests that only a factor of two is required.

C. Lasing in Solar Simulator

Attempts to lase the liquid neodymium system in the solar simulator were not successful. According to Table II, about 10 KW light power is required and the solar simulator provides only 4 KW.

To prove this point, additional light was added by a flashlamp to increase the power from 4 KW to 10 KW.

Since it is difficult to measure absolute values, it was decided to lase first using only the flashlamp and so find the minimum energy (and power) required for lasing. The light from the simulator was added, which should lower the energy (and power) required from the flashlamp. This was indeed the case. Table III gives the comparison.

Based on Table III we estimate that 350 Joules was the electrical energy required to achieve lasing with one flashlamp in the cone of the solar simulator. If the light of the simulator was added, less than 147 Joules of electric energy was required to achieve lasing. This is 42% of the original energy (power), therefore the simulator must have added 58% of the energy (power).

Table III

| Shot # | Voltage KV | Energy Joules | Result L or NL | Shot # | Voltage KV | Energy Joules | Result L or NL |
|--------|------------|---------------|----------------|--------|------------|---------------|----------------|
| 1 | 2.4 | 504 | L | 1 | 2.4 | 504 | L |
| 2 | 2.1 | 385 | L | 2 | 2.1 | 385 | L |
| 3 | 1.9 | 315 | NL | 3 | 1.9 | 315 | L |
| 4 | 1.4 | 171 | NL | 4 | 1.5 | 196 | L |
| 5 | 1.3 | 147 | L | | | | |

D. Summary

Based on our experiments at NLRC

- A. if the shutter opening speed can be set to 0.15 millisecc and
 - B. if the light output of the solar simulator could be doubled
- lasing could, indeed, be achieved.

An alternate approach would be to improve the lifetime of the liquid by a factor of two. The presently used liquid has a lifetime of 150 μ s. We produced at one time a batch of liquid having a lifetime of 280 μ sec, therefore, we know doubling of the lifetime is, in principle, possible. Also, the quality of the cavity can be improved by adding Brewster windows.

We will try to achieve both goals, namely

1. Increase in lifetime
2. Improvement of cavity quality

Our ultimate goal, however, is to be able to produce a liquid with a 300 second lifetime and a lasing threshold of less than 50 Joules electrical (with a 98% output coupler).

VII. FABRICATION OF LIGHTWEIGHT INFLATABLE MIRRORS FOR THE SOLAR PUMPING OF LASERS

As part of our continuing effort to develop inexpensive but large parabolic concentrators for the purpose of pumping both glass and liquid lasers for continuous output, we have developed a ten foot in diameter inflatable mirror capable of concentrating sunlight by a factor of 300 at a focal length of 30 ft. This work was intended as a compliment to an earlier NASA sponsored effort to design centrifugally spun parabolic mirrors and is intended to investigate how one may construct very large but at the same time lightweight solar concentrators for space applications. One of the negative points concerning centrifugally spun mirrors is that their weight still remains appreciable despite the fiberglass technology used in their construction. As will be shown below, inflatable mirrors are much lighter than either glass or epoxy mirrors and have the additional advantage, for space applications, that they are deployable.

The earliest work on inflatable mirrors was done in Russia during the 60's^{5,6}. These studies showed one can produce nearly parabolic deformations in thin sheets of reflective mylar by creating a partial vacuum behind one side of the sheets. Sunlight concentrations of several hundred were obtained with such mirrors and observed problems with wind loads and edge wrinkling near the circular supporting hoops of the membranes were noted. This work was shortly after followed by several investigations in this country^{7,8}. Sunstrand Corporation⁷ developed a 15 kw solar concentrator based on the same approach as used by Umarov⁵ of creating a vacuum behind one side of a reflective polyester film held by a large circular hoop. An important modification of this film distortion process to produce sunlight concentration was made by Taylor⁹ and also discovered independently by us through some research efforts using small parabolic mirror models. In this modification one replaces the need for a vacuum by inflating the space between two membranes attached to a hoop as shown in Figure 25. The resultant lens like configuration has excellent focusing capabilities and has the additional advantages of being very light and also inexpensive compared to other concentrator construction methods.

Our work on inflatable mirrors began in late 1983 with the construction of a small 1.5 foot in diameter model and culminated in the fall of 1984 in a 10 foot diameter inflatable parabolic mirror capable of focusing incoming sunlight to a 6" diameter spot at a focal length of 35 ft. The geometry of this mirror is shown schematically in Figure 26. It consists essentially of a ten foot in diameter polyurethane ring rigidized by fiberglass techniques plus two thin sheets of polyester film attached to the top and bottom surfaces of the ring to form a cylindrical cavity of 5" height and 10 ft diameter. One of the films is transparent (3M Flexiguard 7410) and 0.007" thick while the other has a reflective surface (3M ECP-1) and is 0.002" thick. The transmissivity of the

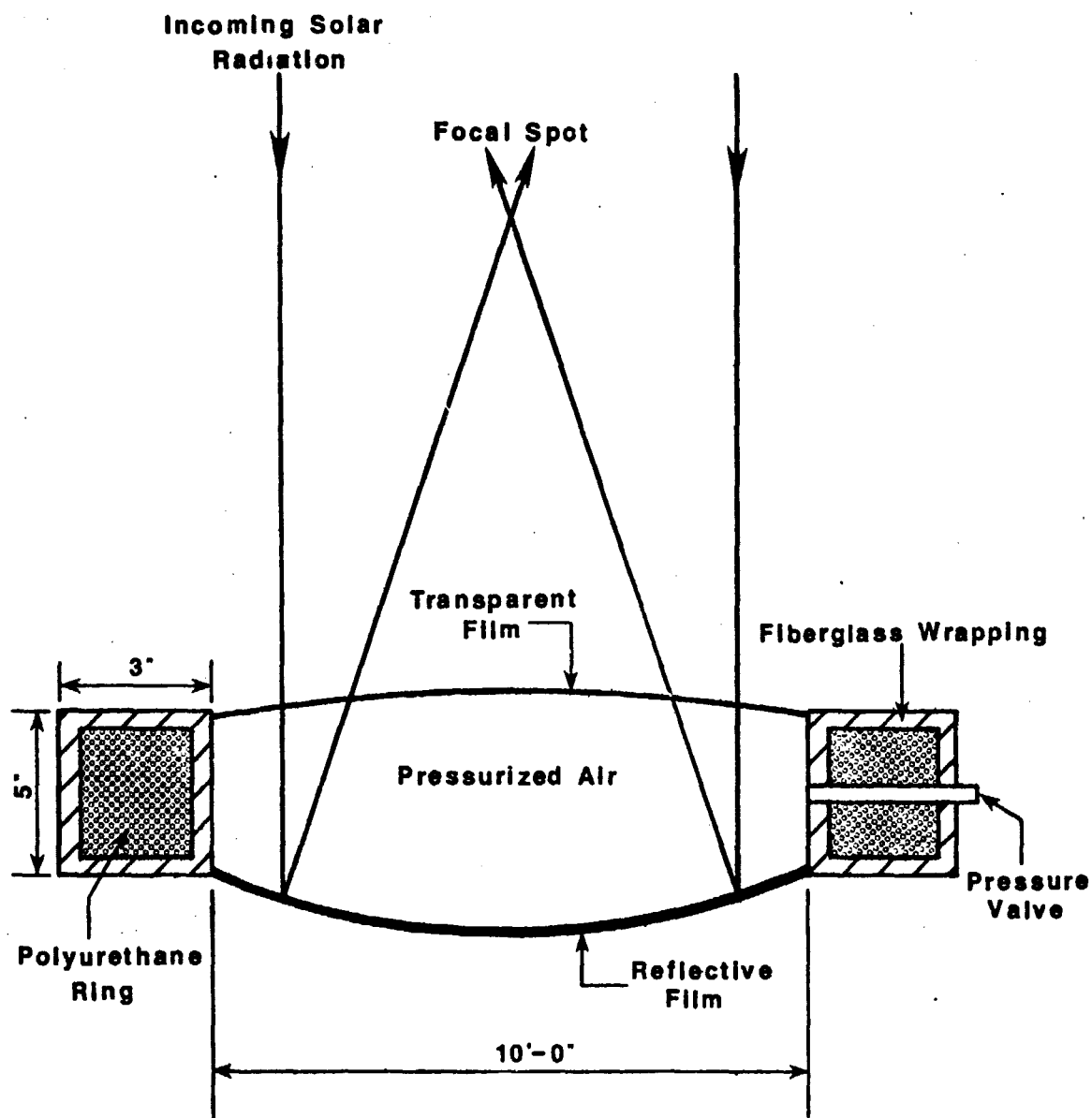


Figure 25: Schematic of an Inflatable Concentrator for the Solar Pumping of Lasers. (Not to Scale)

Possible Commercially Produced 2 Ft. in Diameter Hermetically Sealed
Mirror for Solar Enthusiasts and Amateur Scientists - April 4th, 1985

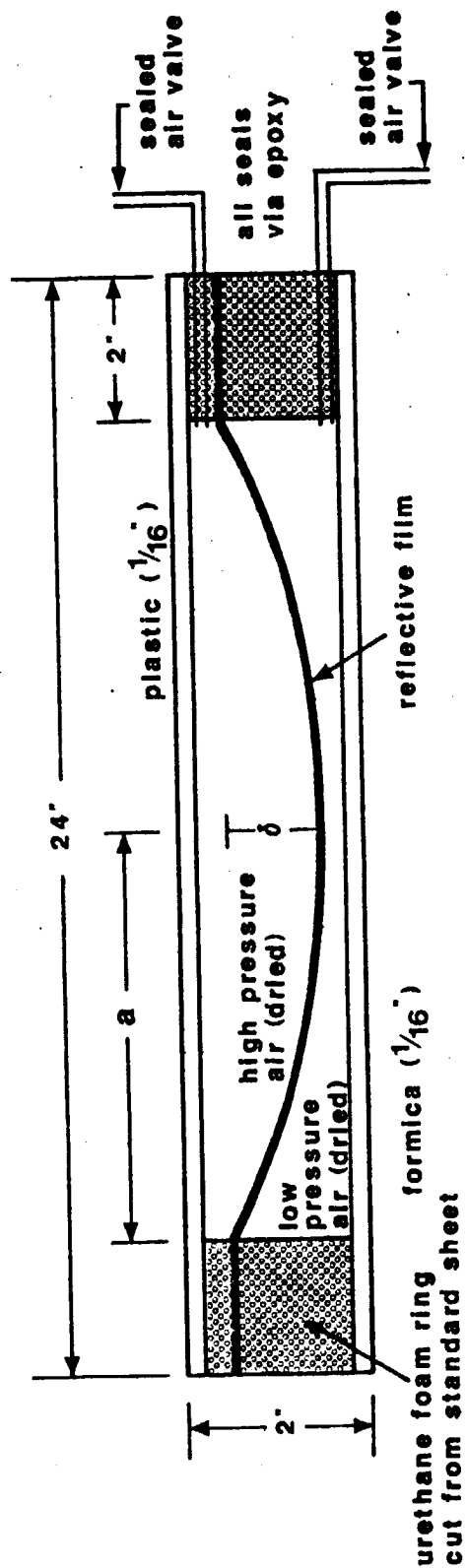


Figure 26: Focal Length $F = a^2/4\delta$, with a - mirror radius,
 δ - maximum membrane reflector
 Example $a = 10"$, $\delta = 1"$ gives $F = 100/4 = 25"$.

transparent film and the reflectivity of the metalized film are stated by the manufacturer to be 90% over the entire solar spectrum. One thus loses some 30% of the incoming radiation. Since the films do not come in widths wider than four feet it was necessary to bond several strips together with adhesive tape. Bonding of the films by either ultrasonic means or by heat are not possible for the particular films used. The ring to which the circular films are attached was constructed by cutting ten sectors of the ring (employing commercially available urethane foam) and then bonding these together using polyester resin and fiberglass matting. Each sector represented 72 degrees of a complete circle and had a cross-section of 3" wide by 2.5" high. The sectors were put together much like two rows of bricks with the joints of the upper row lying on top of the center of the sectors in the lower row. Weight of the entire ring with the attached films is less than 50 pounds and can easily be lifted and oriented by two individuals. Inflation of the cylindrical space between the films is accomplished by means of a valve projecting through the polyurethane hoop. Typical pressures required to produce sunlight concentration at a focal length of 35 ft. was less than 1 psig. Air leakage from the inflated lens configuration was very small, so that reinflation was not required for periods of several days.

Although we did not measure the distortion of the films normal to their planes directly, one knows from analytical grounds, based on the theory for uniformly loaded membranes of zero flexural stiffness¹⁰, that the displacement z is

$$z = z_m [1 - 0.9 (r/a)^2 - 0.1 (r/a)^4] \quad (1)$$

where r is the radial distance, a is the mirror radius and z_m the maximum deflection at the mirror center. Note that z_m for the transparent film is much less than for the reflective film because of their over three fold difference

in thickness. Equation (1) shows that the film deflections are not quite parabolic but that the deformation is very close to that of a parabola near the central portion of the mirror. Our observations using the present mirror at a pressure producing a 35 ft focal length show a 6" diameter focal spot for sunlight. This is only slightly larger than the theoretical value of $F/115$ (where F is the focal length) expected for an ideal parabolic mirror. This fact indicates that the departures from a parabolic shape given by Eq. (1) do not degrade the mirror performance to any large extent. It is also noted that using the present inflatable mirror without a heliostat leads to some off-axis asymmetries in the focal spot shape. Typically one observed an elliptical cross-section for maximum illumination at the focal spot. As long as the angle between the sun direction to the mirror and the line from the mirror to the focal point remained less than about 15 degrees the eccentricity of the focal spot remained small. As in earlier work with membrane mirrors^{5,7,9}, some wrinkling of the reflective film in the vicinity of the supporting hoop was noted. This clearly is the result of trying to have a relatively inelastic flat surface conform to a parabolic surface and cannot be done unless radial cuts are introduced into the film or the film is preformed into a parabolic shape of fixed focal length. We have not had time to pursue these points but can suggest that one way to avoid the wrinkling problem would be to mount sectors of the reflecting film onto a highly flexible rubber membrane leaving small strips between the sectors uncovered by reflecting film. As a result the highly flexible rubber material will stretch sufficiently to avoid the edge wrinkles. Finally it should be pointed out that the distorted reflective film over the inner two-thirds of the mirror surface is smooth to within several wavelengths of light. This follows from the fact that one was able to observe Newton's rings on the back of the reflecting film under inflated conditions. These rings have spacings of several inches and have little curvature.

VIII. CONCLUSIONS AND RECOMMENDATIONS

A good figure of merit for any high power space based solar pumped laser candidate is that it must have a low enough lasing threshold such that it can be lased in the 4 Kw (Xenon arc) solar simulator at the NASA Langley Research Center. The pumping power provided by the simulator is approximately the same intensity that can be provided by large solar concentrators deployed in space. Thus, any lasant requiring a higher intensity (pumping power) would require new technology in solar concentrations not foreseen at this time.

The $\text{POCl}_3:\text{Nd}^{3+}:\text{ZrCl}_4$ liquid laser has the appropriate characteristics which make it an ideal candidate. However, in our attempts to produce the optimal liquid we were successful only once in six attempts to produce the liquid with the required characteristics. The most sensitive characteristic of the liquid is the upper state lifetime of the Nd^{3+} lasant. The optimum value for the lifetime is reported in the literature to be 320 μsec ($\pm 20 \mu\text{sec}$). Our best effort only produced a 280 μsec lifetime while all other attempts produced a mere 140-150 μsec lifetime.

We believe that our inability to routinely produce the liquid with optimal characteristics was due to our lack of adequate facilities for eliminating protic contaminants during the liquid storage and transfer operations. There also seems to be a lack of sensitive diagnostic test for liquid quality during the various preparation stages making it difficult to pinpoint sources of contamination. Once the liquid is finished, the lifetime measurement is a very sensitive means to determining quality. Therefore we recommend that the research on the $\text{POCl}_3:\text{Nd}^{3+}:\text{ZrCl}_4$ laser liquid be continued providing an appropriate source of the liquid can be obtained with adequate facilities for handling and processing the liquid in a water-free environment. Our efforts to

produce an inexpensive, lightweight solar concentrator for space applications is highly successful. We have produced a 10 foot diameter large focal length concentrator weighing only 50 lbs. This mirror produced a 6 inch diameter focal spot with a total irradiance of 3.5 kilowatts. This represents a vast improvement from our earlier attempts with spin-cast fiberglass composite mirrors weighing 400 lbs.

Our inflatable concentrator is a viable candidate for large scale solar concentrators which are deployable in space.

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